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**CONSOLIDATION AND ADHESIVE REPAIR OF VOLCANIC TUFF  
CASE STUDY: CONSERVATION OF VOLCANIC TUFF AT THE OLD  
STONE CHURCH OF MISSION SAN JUAN CAPISTRANO,  
SAN JUAN CAPISTRANO, CALIFORNIA**

Evin Hewett Erder

A THESIS

in

The Graduate Program in Historic Preservation

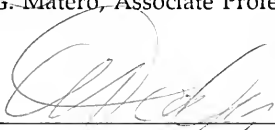
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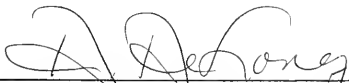
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# INTRODUCTION

Stone artifacts and structures begin to deteriorate at the moment of their completion, and exposure to the environment; their deterioration accelerates over time, usually resulting in the gradual disaggregation, cracking and loss of material. The porosity and permeability of the stones allows water in the liquid and vapor phase to penetrate and cause a variety of decay mechanisms that accelerate their deterioration. The effects of the deterioration process can be delayed indeterminately, however, by selecting suitable protective or consolidating materials. Appropriate selection of materials for stone conservation requires the careful design and application of both laboratory and field tests to characterize the physical and chemical properties of the stone, and evaluate the performance of possible protective or consolidating materials. Knowledge that the effects of the deterioration of porous materials can be delayed through the application of suitable consolidants or protective materials is one of the most important factors contributing to the conservation of stones of cultural and historic value.

The use of natural and synthetic materials to intervene in deterioration processes to delay stone decay has been common practice since classical antiquity. Ancient Greek and Roman writers, including Vitruvius, recorded efforts made to intervene in the decay of stones. Artists in the Medieval and Renaissance periods applied protective materials to stone sculptures exposed to the weather. Stone conservation as a specialized science, however, began only recently, at the end of



the 19th-century. It is now recognized that testing programs designed to assess the effects of both natural and synthetic materials on stones can minimize the damaging effects of these materials, and delay deterioration.

*This study focuses on the results and findings of an experimental program designed to conserve highly porous stone with poor mechanical properties.* The decision to conserve the volcanic tuff stones at the Stone Church of Mission San Juan Capistrano in California in December 1994 defined the scope of the treatment program. This stone, used for the interior cornices, pilasters, doorways and other decorative elements of the church has deteriorated rapidly, and requires the application of appropriate conservation measures that will retard further deterioration. The penetration of water into the stone, and continuous wet-dry cycling represents the major cause of deterioration. Internal stresses caused by water penetration and salt crystallization have led to the rapid disaggregation and cracking of the stone.

Recent studies on the conservation of porous stone such as sandstone and tuff have shown that alkoxysilanes and epoxy resins can improve strength and resistance to deterioration, while causing minimal change in the permeability, water vapor transmission, and appearance of the stones. These two consolidation systems were therefore selected, and tested as possible consolidants for the tuff, in combination with an epoxy resin as an adhesive for the cracks. The experimental program, designed to test the performance of these materials, showed that consolidation with either epoxy resin, or ethyl silicate, and injection of the epoxy adhesive into cracks can indeed increase the stones' resistance to





deterioration. Both the consolidants and the adhesive resin caused minimal change in the permeability, porosity, and appearance of the stones.

The research on epoxy resins in this study is based on the results of research carried out W. Domasłowski at the Scientific Laboratory for Stone Conservation in Toruń, Poland; R. Cavaletti, L. Lazzarini, and G. Marinelli in Italy, and W. Ginnel, C. Selwitz, and P. Kotlik at the Getty Conservation Institute in Marina del Rey, California. The characterization of alkoxysilanes used for stone conservation is based primarily on the research compiled by Isil Öztürk from numerous sources in her thesis, "Alkoxysilane Consolidation of Stone and Earthen Building Materials." The format for the thesis is modelled after the format developed by Anne Brackin in her thesis, "A Comparative Study of the Effects of Applying Acrylics and Silanes in Sequence and in Mixture, with a Case Study of the Column in the Convento of Mission San Jose Y San Miguel de Aguayo, Texas."

The conservation of porous stones exposed to the environment can only be achieved through a phased program, involving both laboratory and field tests, and a program for their conservation, monitoring, and maintenance. The conservation process begins with the documentation, and comprehensive survey of the conditions of the stones. The preliminary survey of the character, nature and conditions of the stones is followed by extensive laboratory studies on the physical and chemical properties of the stones, the major causes of their deterioration, and their deterioration mechanisms. Based on the results of these



studies, possible materials for conservation may be selected, and tested through suitable laboratory and field tests. Experimental testing programs are designed both to analyze, and evaluate the properties of the stone treated with these materials. After studying, assessing and evaluating the performance of the conservation materials in the laboratory, the same materials must be applied to a representative test area on site to monitor and evaluate the performance of the materials on stones during their exposure to the environment. The materials and application methods that appear to delay deterioration without damaging the stones may then be applied to the stones at the site. In the conservation of porous stones, whether artifacts or stone structures, the design of the experimental program and appropriate selection of materials and methods for the consolidation and/or protection of the stones is critical to finding the most suitable means for conserving the stones.



# CHAPTER ONE

## HISTORY, CHARACTERIZATION AND USE OF MATERIALS AND FOR STONE CONSERVATION

### 1.1 OVERVIEW

The conservation of stone, practiced since classical antiquity, and written about by classical authors, became common practice in the Medieval era and the Renaissance. Vitruvius writes in the *Ten Books of Architecture* that "naked sculptures were protected with wax melted and mixed with little oil."<sup>1</sup> Technical treatises from the tenth to the seventeenth centuries include descriptions of materials used for the protection of stone sculptures. Andrea Pisano's technical manuals, for example, include a description of *cera colla*, a mixture of wax and resin. The artist applied this resin as a protective varnish on painted marble sculptures. Analytical studies have shown that this protective material was used on the marble facade of the Orvieto cathedral in the fourteenth century.(Rossi-Manaresi 1973, 83) The sixteenth century Marcianna manuscript reports another recipe for varnish intended for every kind of work on all materials."(Rossi-Manaresi 1973, 83) The recipe for this varnish included sandarac, nut oil, incense and potash alum, used both on painted and unpainted stone surfaces. Physical analyses of stone sculptures and artists' technical records dating to the fifteenth and sixteenth centuries provide insight on the materials used for stone protection and consolidation during that period.(Rossi-Manaresi 1973, 83)



A study by R. Pellizer and R. Rossi Manaresi cited some documentary evidence on protective coatings used in the fifteenth century in Bologna. Their study focused on protective coatings applied by Jacopo della Quercia on sculptures in the major portal of the Church of San Petronio in Bologna in the fifteenth century. The study revealed that the protective coatings contained hydrocarbons, fatty acid esters, fatty acids and alcohols, the essential constituents of natural waxes.<sup>2</sup> Artists in classical antiquity used a mixture of resin and wax, similar to the wax applied to the sculptures of Jacopo della Quercia, as water repellents for stone surfaces. In the first century A.D., Dioscorides provided a record of the application of such protective coatings to stone in his book *De Materia Medica*.(Rossi-Manaresi 1973, 86) *Cera colla*, another type of mixture of resin and wax, appears in many technical manuals beginning in the fourteenth century. A Venetian manuscript from the fourteenth century describes a varnish containing turpentine, mastic and wax. A similar recipe appeared in two Florentine manuscripts, from the late fourteenth century and mid-fifteenth century.(Rossi-Manaresi 1973, 86) Several technical manuals describe recipes for a mixture of wax and resin used as waterproof cements.(Rossi-Manaresi 1973, 87) A book of secrets by Timoteo Rosello dating to the sixteenth century contains a recipe for "*far crescere la cera*."(Rossi-Manaresi 1973, 87) This resin is a wax composed of a mixture of colophony, honey, wax and mutton tallow applied to objects as a hydrophobic agent. Recipes for mixtures of resin and wax, well known during the Medieval and Renaissance periods, were commonly used as varnishes.(Rossi-Manaresi 1973, 87) These mixtures, however, also served as basic





recipes for protective coatings for stone. Evidence of the presence of coatings composed of these materials on stone objects suggests that the hydrophobic properties of these coatings may have been common knowledge.(Rossi-Manaresi 1973, 87)

Scientific examination of decay mechanisms and consolidants began in the mid-nineteenth century.<sup>3</sup> Many conservation treatments applied previously as superficial gluing, waterproofing, or shallow pore-blocking treatments appeared both ineffective, and severely damaging to stones; subsequent treatments of the same objects with these materials was either extremely difficult or impossible. Among the treatments used in the nineteenth century, lime water, lime-casein, lime-tallow and barium hydroxide provided protection for stone and lime stucco. Stone consolidation techniques developed by scientists and conservators in the 19th-century, however, usually attempted to consolidate stones in one step. Conservators conceived such chemical treatments as a simple means to improve the grain-to-grain cohesion of stones and to protect them against the environmental conditions for an extended period.<sup>4</sup> Scientists and conservators have since redefined stone consolidation as a process involving a sequence of treatments. The term "stone consolidation" refers to all procedures that reestablish grain-to-grain cohesion in stones and provide long-term protection against environmental conditions. At first, testing programs for many of these materials only assessed their short-term effects. Later such treatments proved to be incompatible with, and damaging to the stones. As a result, scientists and



conservators began to design more rigorous testing programs to assess the performance of conservation materials, simulating field conditions as closely as possible.

Consolidants, even when carefully selected, often present limitations and drawbacks in their application and long-term effects on stones. Today, the use of consolidants for stone conservation requires the application of a comprehensive testing program. The testing program requires two parts: (1) laboratory tests, and (2) field tests. The laboratory testing programs are designed to assess the physical and chemical properties of stone consolidated with the selected consolidants (i.e., depth of penetration, appearance, grain-to-grain cohesion, water vapor permeability, compressive strength), and various application conditions and methods. The field tests assess the performance of the consolidation system in field conditions. The laboratory program first assesses the consolidants under specific conditions (i.e., temperature, relative humidity, soluble salts, sulfur dioxide), and through various application methods. Based on the results of the tests, possible consolidants are tested through a field testing program to correlate the laboratory tests with the field tests. A consolidant that appears to impart the appropriate properties for consolidation in the laboratory may require the use of complex and labor-intensive application procedures and present health hazards. Each consolidant has its advantages and disadvantages; it is critical to weigh the pros and cons of each treatment in relation to the specific characteristics of the stone and its physical condition in selecting an appropriate consolidation method.



Protective coatings and consolidants may accelerate rather than delay deterioration for two reasons: (1) water enters through macroscopic cracks, but is prevented by the treatment from evaporating from the pores to the surface of the stone; (2) the treated layer differs in moisture transmission and thermal movement properties from the underlying stone that may lead to more shear failure.<sup>5</sup> It is necessary for treatments to penetrate the stone deeply enough, and maintain the same permeability and thermal movement properties of the stone. Consolidants must also increase the stone's resistance to further deterioration by increasing "the stone's tensile strength and/or a modification of its pore structure." (Ashurst and Dimes 1977, 60) Consolidants can also prevent further deterioration caused by salt crystallization by encapsulating the salts in the resin and/or making the stone more resistant to salt damage. Selection of an appropriate protective consolidant requires careful consideration and evaluation of the long-term effect of the consolidating materials on the stone. Evaluation of possible treatments through an experimental program, in the laboratory, and in the field is essential to the appropriate selection of consolidation and/or protective systems.



## 1.2 CHARACTERIZATION OF MATERIALS AND METHODS USED FOR STONE CONSERVATION

Stone consolidation consists of the deposition of a new, durable binding material within the pore system to alter the physical or mechanical properties, such as the compressive strength, modulus of rupture, elasticity and abrasion resistance of the stone. The consolidant must "penetrate deeply and evenly into the stonework and then solidify."<sup>6</sup> The viscosity of the liquid "must not be much more than that of water." (Ashurst and Dimes 1977, 60) It is possible to achieve the appropriate viscosity of the solution by the dissolution of the resin in a low viscosity solvent or by using liquids consisting of low molecular units (i.e., monomers) which subsequently react with the stone to produce a larger molecular network (i.e., a polymer). It is usually necessary to apply the consolidant selected for the treatment "intermittently over a period of several hours to achieve adequate penetration," (Ashurst and Dimes 1977, 60) and even distribution of the consolidant. The timing of the application method has a direct effect on the penetration and distribution of the consolidant within the stone structure. If the solution sets too slowly, it may evaporate or spread too thinly through the stone. If the solution sets too rapidly, it will prevent penetration.

Deep penetration, and even distribution of the consolidant within the stone, and the porosity and permeability of the stone after treatment provide mechanical strength to the stone while causing minimal damage to the stone. As the solvent evaporates during the application process, the resin may migrate back to the





surface. The composition of the solvents and resin, and the application method used influence the degree of penetration and solidification of the resin at the surface of the stone. Testing various resin formulations, and application methods prior to application will help determine the consolidation system that causes the least damage to the stone. The consolidant must also allow the movement of liquid and water vapor through the porous structure of the stone, and minimize the crystallization of salts within the stone. The stone consolidation system must achieve the following:

- ◆ substantial penetration of the consolidating solution or consolidant (i.e., deposition within the weathered zone and underlying layers);
- ◆ minimal reduction of water vapor permeability;
- ◆ absence of deleterious chemical and physical interaction between the consolidant and the building stone;
- ◆ absence of deleterious chemical and physical interactions between the consolidant and the building stone;
- ◆ minimal hazard to health and/or safety;
- ◆ minimal or no aesthetic alterations;
- ◆ creation of a continuous hardness profile.<sup>7</sup>

Consolidation methods for stone conservation are normally classified as (1) inorganic, and (2) organic consolidants. Inorganic consolidation processes derive from chemical processes that deposit inorganic material in the stone. In selecting an inorganic consolidant, the conservator must consider the possible formation of



by-products with undesirable properties. Alkali-silicates, for example, yield alkali soluble salts that may induce deterioration processes. Barium hydroxide may also form a white, powdery by-product on the surface of the stones. Lime water usually forms minor by-products, but requires labor intensive application procedures. Laboratory and field tests simulating field conditions, however, can help determine how the consolidant interacts with the stone, and whether by-products will form on the surface of the stone.

Organic consolidants introduce an organic compound into the stone and impart grain-to-grain cohesion. The depth of penetration of the organic molecule depends on the size of the molecules and their deposition within the structure of the stone. Alkoxysilanes and thermosetting resins such as epoxy resins can achieve deep penetration if used in a suitable mixture. Alkoxysilanes are monomers that polymerize *in situ*. The reaction of the silane with water and the loss of alcohol during evaporation drive the curing process. The consolidated stone always remains permeable to water. Besides imparting grain-to-grain cohesion, these silica forming organic compounds may also impart a degree of water repellency to the stone. In these compounds, the ethyl silicate derived from methyl groups bonds directly with the silicon atom form a partly organic compound. Consolidants that form volatile by-products, such as ethyl silicate and related compounds, do not present this problem. Silicones used for stone consolidation are usually the ethyl-methyl-silane type. Low molecular weight synthetic organic monomers such as epoxies can also provide satisfactory results



due to their reliable thermosetting properties.

Consolidation with synthetic organic resins consists of the deposition of the resin into the stone, and the formation of a polymer network that supports and binds together loosened particles of stone. It is possible to introduce synthetic resins into the stone by applying polymers, prepolymers, or monomers. The simplest method for introducing a resin into a porous material is by dissolving the resin in an appropriate solvent, and applying the mixture to the object. The major factors that determine how an organic consolidant reacts with a particular stone include the molecular size of the resin, the types of solvents used, and the application procedures. If the resin does not penetrate the material evenly and deeply enough and begins to polymerize too soon, the resin may migrate back to the surface during evaporation of the solvent and the curing process. After repeated exposure to environmental or weather conditions, the consolidated surface layers may then crack and peel off.

The use of a suitable combination of resins, solvents and application methods can reduce the discoloration and reverse migration of organic consolidants considerably. Consolidation with prepolymers such as some epoxy and acrylic resins appears to mitigate many disadvantages associated with the use of resins for consolidation. Acrylic resins may be diluted with reactive solvents that do not evaporate during polymerization. Epoxy resins are monomers that polymerize, and form cross-linked polymers within the stone. Consolidation with some low molecular epoxy resins can achieve deep penetration due to their low



viscosity, and thus reduce the risk of discoloration. The type of epoxy resin, hardener and solvents used determine the polymerization reactions, and the distribution and interaction of the polymer with the stone.

Inorganic consolidants impart mechanical strength, but often do not restore the strength of the stone to a level equivalent to the strength of the stone before deterioration. Organic consolidants generally impart high mechanical properties, but the consolidants themselves often present drawbacks in their application, and the degradation of the consolidants with exposure to oxygen and ultraviolet light. The absence of standardized procedures for evaluating stone consolidants, however, represents the most significant limitation in the assessment of various materials and systems for stone consolidation. R.I.L.E.M. (Reunion International de Laboratoires d'Essais et de Recherches sur Materiaux et de Construction, in France) and the B.R.E. (Building Research Establishment, in Great Britain) have initiated efforts to codify procedures for the evaluation of conservation treatments. Although both organizations have succeeded in establishing procedures for assessing laboratory tests on consolidants, they have had little success in natural exposure trials designed for this purpose. The ability of chemical consolidants to impart stones with significant resistance to deterioration nevertheless suggests the need to pursue standardization of procedures for the evaluation of stone consolidants in field applications.

The definition of acceptable criteria for stone consolidation has been a major subject of debate since the scientific investigation of the use of consolidants





in the conservation of objects of historic and cultural value began in the mid-nineteenth century. As early as 1921, Heaton defined the characteristics of an ideal consolidant.<sup>8</sup> These criteria are, for the most part, still valid. The criteria for the perfect consolidant defined by Heaton include the following:

1. The consolidant must penetrate deeply and evenly into the stone and remain in the stone after curing;
2. it must not concentrate on the surface to form a hard crust, but must also harden the surface;
3. it must not discolor or alter the original appearance of the stone;
4. it must expand and contract uniformly with the stone to prevent cracking and flaking;
5. it must be non-corrosive and not harmful to use;
6. it must be economical in material and labor application;
7. it must retain its preservative effect indefinitely.

In addition to the above criteria, a stone consolidant is required to meet the following requirements:

8. it must regulate the diffusion of water and water vapor through the stone;
9. it must constitute a screen against atmospheric pollutants, dust, biological agents and wind erosion;
10. it must not deposit any solid matter within a reasonable temperature range;
11. it must not take on a crystalline state and thus introduce the danger of surface disintegration owing to the growth of crystals;
12. it must not depend for its preservative properties on a reaction within the stone substrate itself.(Amoroso and Fassina 1983, 255)

One of the most important factors in determining the suitability of the application of a consolidant is the open porosity of the stone. In sandstones, for example,



natural cements bind sand grains together in varying degrees. The cement may form a single contact film over the grains or fill the pores between the grains. The dissolution of the cement as the stone weathers often results in its deposition on the surface of the stone, and the disaggregation of underlying layers of stone. Organic silicates consolidants can bond with quartz grains in the sandstone and bind the grains together. The removal of soluble salts from the stone before the application of an organic silicate ensure the grain-to-grain cohesion and permeability of the stone after consolidation.<sup>9</sup> If the stone has become too fragile for the removal of salts, it may be necessary for the consolidant to encapsulate the salts to prevent further deterioration by salt crystallization. Regardless of the condition of the stone, however, the consolidant must allow the diffusion of water and water vapor through the porous structure of the stone, impart grain-to-grain cohesion and mechanical strength and cause minimal alteration in the appearance of the stone.

Consolidation of stone often yields variable results due to the physical and chemical inhomogeneity of most stones. Each specific stone will respond differently to similar consolidation techniques. The travel routes of moisture and the presence of soluble salts within the stone often create hidden variables in the responses of stones to various treatments. The complexity of the interaction of chemical substances with stones requires an understanding of the most significant variables affecting the deposition, and curing or polymerization of the consolidant in the stone. The testing program must therefore analyze, and assess the most



important physical and chemical alterations that occur after consolidation, and the effects of the environment on the physical properties and appearance of the stone.

Testing of consolidants through laboratory programs and field applications has limited the range of consolidants recommended for stone conservation considerably. In the past, linseed oil, waxes and metallic stearate have been found to provide a measure of consolidation. Linseed oil and waxes, however, are generally not used for stone consolidation any longer, and metallic stearates have become unpopular due to their corrosive action on many types of stones. Substances such as fluorosilicates of magnesium, zinc or aluminum, acrylic resins, ethyl silicates, and epoxy resins can provide good consolidation to most types of stones. By far, the most popular consolidants are alkoxysilanes.(Dukes 1972, 434) It is also common practice now to apply these materials with silane water repellents, either separately or in the same organic solvent vehicle.(Dukes 1972, 434) Alkoxysilanes hydrolyze in the presence of atmospheric moisture to precipitate form silica ( $\text{SiO}_2$ ). Consolidation occurs by the deposition of silica in the pore structure. The major disadvantage of siliconesters is their low depth of penetration.(Dukes 1972, 436) Acrylic and epoxy resins are also applied in the field for consolidation quite regularly, but still require further testing to determine the most appropriate formulations for different types of stones and weather conditions.

A critical criterium for consolidants to work, although still controversial, is the similarity of the properties of the consolidant to the stone to be



consolidated. In the past, scientific studies on consolidants found many advantages to the application of consolidants having the same or similar chemical, physical, and mechanical properties to those of the stone. Following this principle, conservators began applying inorganic compounds, i.e., barium, calcium, strontium hydroxide, water glass and water soluble fluorosilicates. Most of the results were disappointing, however. In some instances, these substances can fill and consolidate the stone surface, and a few years later the indurated surface detaches, exposing underlying layers of disaggregated stone. The failure in the application of these inorganic consolidants led to reconsideration of the application of synthetic organic resins. The use of these resins opposes this principle. There are many scientists and conservators who continue to oppose the use of these resins, and only apply inorganic compounds in stone consolidation.<sup>10</sup>

To date, there are no consolidation procedures that are completely and practically reversible. Each consolidation material requires the permanent application of an extraneous material to the object. Consolidation materials and their by-products generally have chemical, physical and mechanical characteristics different from the stone. The materials applied most frequently in current practice, however, may be classified as follows:





## Consolidation materials<sup>11</sup>

### Advisable consolidants

The following consolidants have been found to cause minimal alteration of stones:

- a. ethyl silicates
- b. alkyl-tri-alkoxysilanes
- c. mixtures of the above
- d. alkyl-ethyl-polysilanes (totally or partially polymerized)
- e. epoxy resins
- f. acrylic resin solutions
- g. barium hydrate (baryata)
- h. lime water

### Inadvisable consolidants

The following consolidants have been found to cause unacceptable alteration of the stones:

- a. sodium and potassium silicates (cause the formation of soluble salts as by-products);
- b. sodium and potassium aluminates;
- c. zinc and magnesium fluorosilicates (have low depth of penetration that causes formation of soluble salts as by-products, often due to the presence of zinc or magnesium sulfate impurities).



Among the consolidants studied thus far for stone consolidation, epoxy resins and ethyl silicates, used extensively for the consolidation of porous stone in the field, have demonstrated their ability to increase grain-to-grain consolidation, improve mechanical strength, and cause minimal change in the permeability and porosity of stones. Due to their capacity to impart high mechanical strength, while causing minimal change in the porosity of stones, these resins provide particularly good consolidation for stones having poor mechanical properties.

In developing the conservation program for the tuff blocks at the Old Stone Church, an aliphatic epoxy resin, EPONEX 1510 (Shell Chemical) and an alkoxysilane, CONSERVAR OH (ProSoCo) were selected as two possible treatments for the consolidation of the stones, and an epoxy resin for the adhesive repair of the deep cracking in the stones. Application of these consolidants in the field have provided many good results. Both consolidants have low viscosity, high depth of penetration, increase grain-to-grain cohesion, and if applied under suitable conditions, and with appropriate methods cause minimal change in the appearance of the stones. Two systems thus became the focus of the testing program for the volcanic tuff blocks at the Old Stone Church: (1) consolidation with epoxy resin and adhesive repair with ethyl silicate; (2) consolidation with ethyl silicate and adhesive repair with epoxy resin. Epoxy resins and alkoxysilanes used for the stone consolidation are characterized in the following two sections.



### 1.3 CHARACTERIZATION OF EPOXY RESINS USED FOR STONE CONSERVATION

The use of synthetic organic polymers as stone consolidants is a recent development. Experimental research on synthetic polymers such as epoxy resins for stone consolidation began in the 1960s. Although their long-term effects on stone are not well-known due to the recent inception of their use as stone consolidants, and limited application to stone, their application for stone consolidation has provided successful results. Synthetic polymers form by the polymerization of monomers with low molecular weight. Epoxy resins are thermosetting organic resins that polymerize at a low temperature range, and can therefore provide good consolidation in field conditions. The monomers penetrate the stone and polymerize, forming a three-dimensional network of polymers in the stone. Since the 1960s, conservators and scientists have examined the application of epoxy resins for consolidation of limestone, sandstone and marble objects. Epoxy resins have provided favorable results in stone consolidation primarily due to their deep penetration, durability, good adhesion, and high mechanical strength.<sup>12</sup> Epoxy resins are insoluble once they set.

Epoxy resins have several advantageous properties for stone consolidation. Epoxy resins can cross-link at room-temperature without forming by-products. The reaction between the epoxy group - CH - CH<sub>2</sub> and the aminic hydrogens







has enough free energy for the reaction to be almost complete at temperatures higher than 5 to 10°C.<sup>13</sup> The monomers, depending on their structure and molecular weight, are liquids, brittle, and/or thermoplastic solids. Careful mixing of the monomers in stoichiometric ratios with substances containing more than two amine hydrogens, changes them into insoluble cross-linked polymers. This reaction does not form by-products and the volume of the polymer is practically equal to the total amount of reagent volumes.(Marinelli 1972, 573) Because of cross-links and high-density and stability, the mechanical properties of hardened products are generally high.(Marinelli 1972, 573) Epoxy resins can therefore improve the mechanical properties of stones after correct hardening. Epoxies have good adhesive properties, water resistance, and chemical stability.

An epoxy system consists of an epoxide monomer and a curing agent or hardener that modifies the physical and chemical structure of the resin. The curing agent transforms the resin from a liquid monomer into an insoluble cross-linked polymer. During hardening, the resin normally does not release by-products. Most frequently used curing agents include primary, secondary and tertiary amines, amides, Lewis acids, phenols, Lewis bases, and inorganic hydroxides.<sup>14</sup> Although it is possible to induce hardening at room temperature, some amines require higher temperatures. Aliphatic amines and amides, for example, are for room temperature use, whereas aromatic amines and acid





anhydrides require high temperature curing.<sup>15</sup> A resin and hardening agent with low molecular weights and low curing temperatures can achieve deep penetration in porous stones.<sup>16</sup>

Epoxyes are generally too viscous to achieve deep penetration in deteriorated stone. It is possible, however, to reduce their viscosity by adding organic solvents to the resins. The choice of solvents for achieving low viscosity is very important. The solvent composition affects the reaction between the epoxy compound and amine, and the interaction between the resin components and stone. The solvent composition also affects the penetration, film formation, adhesion, color stability, gas permeability, and other properties critical to the performance of the consolidant. A solvent with hydroxyl groups (-OH) speeds up cross-linking, while a solvent with a carboxyl group (>C=O) in the molecule slows the reaction down.(Kotlik, Justa, Zelinger 1983, 77)

The two main drawbacks of epoxyes are their tendency to discolor upon exposure to light and their insolubility in ordinary solvents after setting. When exposed to sunlight many epoxyes chalk and form a white powdery surface.<sup>17</sup> Epoxyes, if too viscous, can fill pores completely, and prevent air and water vapor transmission through the treated stone. Stresses caused by differential thermal expansion of the epoxy can cause the stone to fail. Riederer argues that stone consolidation with polymer materials works well for a considerable period, but no more than twenty years.<sup>18</sup> Discoloration, loss of tensile strength, and brittleness are common symptoms of the deterioration of polymers. In support



of this claim, Riederer cites examples of different types of deterioration mechanisms observed in stone structures in Germany consolidated with organic polymers.(Selwitz 1991, 91) Deep channel erosion caused by rainwater occurred in several types of stones consolidated with organic polymers within ten years of treatment.

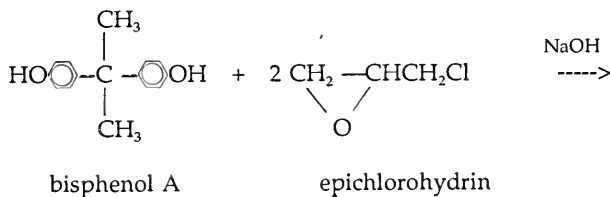
Although epoxy resins can cause considerable damage to stones, recent studies have shown that epoxy resins can also provide stones with resistance to deterioration while causing minimal damage. The use of aromatic and aliphatic resins for consolidation or adhesive repair of porous stones exposed to outdoor conditions, examined in Poland, Italy and the United States, have provided successful results. Aromatic resins, based on bisphenol A diglycidyl ethers, studied by conservators and scientists since the 1960s, can improve grain-to-grain cohesion, increase the mechanical strength, and maintain the water vapor permeability of the stones. More recent studies by Wieslaw Domaslowski, Petr Kotlik, G. Marinelli, L. Lazzarini, K. Lal Gauri, Charles Selwitz, and William Ginnel have shown that aliphatic epoxy resins, if applied correctly, can provide successful results. It is essential to select the proper type of amine, solvents, and to determine the proper stoichiometric ratios for the epoxy system. The method used in applying the epoxy to the stone also affects the results of the treatment. Certain application methods developed for epoxy resins, although usually cumbersome and labor intensive, have provided good consolidation in outdoor environments.



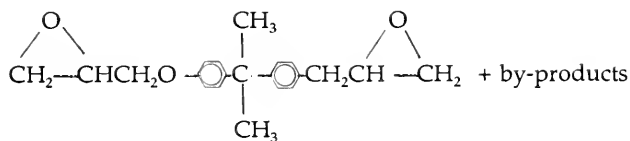
### 1.3.1 CHEMISTRY OF EPOXY RESINS

Epoxy resins are polymer-forming systems containing two principal chemical components that interact to produce cross-linked polymers.<sup>19</sup> Polymerization occurs without the formation of by-products, and generally with less than 5% bulk shrinkage. The high reactivity of appropriate solvents enables the resin to solidify at low temperatures (i.e., at or near ambient temperature). (Selwitz 1991, 13) Mechanical hooking and covalent bonding can also play a significant part in imparting adhesive properties to epoxies. The major mechanism for adhesion is the sharing of electrons between the polymer and the substrate (i.e., coordinate bonding). (Selwitz 1991, 13)

Experimental studies on epoxy resins for stone conservation have focused primarily on the formulation and application of aromatic bisphenol A and aliphatic resins. The epoxy resin most commonly used in studies on stone consolidation by Domaslowski, Lazzarini, Marinelli, Lal Gauri and others is the aromatic epoxy compound, bisphenol A diglycidyl ether (Equation 3). This resin is produced by the condensation of epichlorohydrin and bisphenol A.







diglycidyl ether of bisphenol A

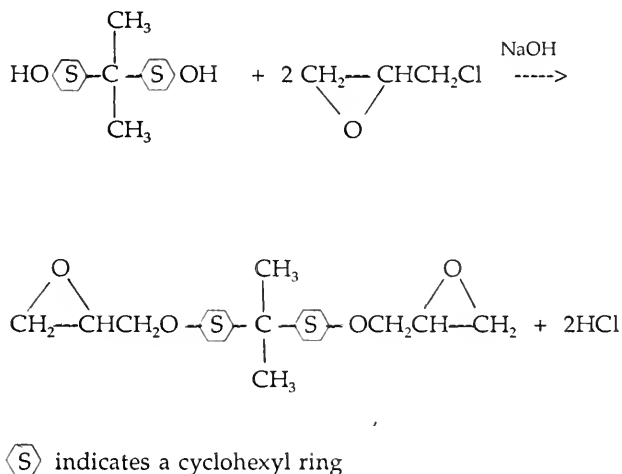
Epoxy resins must contain less than 10-15% non-volatile material corresponding to approximately 10cP viscosity, to provide high depth of penetration.<sup>20</sup> Such a low, non-volatile material presents two contrasting factors. The low viscosity of the resin ensures even distribution and water vapor permeability, but the solution may become too weak for proper consolidation, especially if applied to a porous and degraded material.(Marinelli 1975, 576) Furthermore, aromatic resins do not guarantee resistance to discoloration upon exposure to sunlight.(Marinelli 1975, 576) Bisphenol A epoxy resins are also hydrophobic both before and after consolidation and can inhibit the penetration of the solution into a humid stone.(Marinelli 1975, 576) The chemical composition of the epoxy system and application method therefore have a direct influence on the degree of discoloration and hydrophobic properties of the stone.

A new type of epoxy resin has now been derived from bisphenol A by hydrogenation to 2,2 - di (4-hydroxycyclohexyl) propane and the reaction of this





compound with epichlorohydrin.<sup>21</sup> The reaction of the bisphenol A molecule with hydrogen results in the conversion of the rigid benzenoid structures into more flexible cyclohexyl rings.(Selwitz 1991, 16) This molecule reacts with an epichlorohydrin molecule and yields a cycloaliphatic molecule, much bulkier than the bisphenol A glycidyl ethers.(Selwitz 1991, 18) This linear, bulkier, and more flexible molecular structure provides the resin with lower viscosity, and higher light stability than aromatic resins. The chemical reaction that results in the formation of the aliphatic difunctional epoxy monomer, butanediol diglycidyl ether, is summarized as follows:



This aliphatic difunctional epoxy resin mixed with a cycloaliphatic polyamine



This aliphatic difunctional epoxy resin mixed with a cycloaliphatic polyamine curing agent has very low viscosity, approximately 10cP, and is very hydrophobic before cure.<sup>22</sup> Due to its aliphatic structure, this resin also has good resistance to yellowing.(Marinelli 1975, 577) After hardening, however, the polymer has low strength and low resistance to chemical attack.(Marinelli 1975, 576) Cycloaliphatic amines are the most sensitive of all the amines to attack by atmospheric carbon dioxide.(Marinelli 1975, 576) At room temperature, primary aliphatic and cycloaliphatic amines react easily with carbon dioxide and yield amine-carbonates.(Marinelli 1975, 576) This reaction often becomes visible as a whitish powder on the surface of the treated stone.(Marinelli 1975, 577)

In a series of experimental studies on epoxy resins, Marinelli (1975) found that the use of a mixture of aliphatic epoxy resins with aromatic amines eliminates some disadvantages associated with aliphatic epoxy resins. Aromatic amines provide epoxy resins good resistance to chemical attack.(Marinelli 1975, 577) Marinelli studied the increase in the resistance of several mixtures of aliphatic resins with aromatic amines to chemical attack. Marinelli diluted the resin and amine with a solvent mixture consisting of water and very polar organic solvents until the resin reached a 10cP viscosity at 25°C.(Marinelli 1975, 578) Because of its low viscosity and hydrophobic properties, natural stones, bricks, and mortars can absorb this mixture easily.(Marinelli 1975, 590) The mixture also allows intervention 24 hours after application by washing with a suitable solvent.(Marinelli 1975, 590) This resin, reversible within 24 hours after its



application, provides a suitable means for consolidating deteriorated stones exposed to atmospheric carbon dioxide, water and sunlight. A typical example of an aliphatic resin is Eponex 1510 (Shell Chemical). Although Shell has not yet published specifications for this resin, scientists at the Getty Conservation Institute have examined this resin in experimental programs to test various methods for its application in stone conservation.<sup>23</sup>

Epoxy resins have been considered "second or last choice materials" by most conservators because of their irreversibility.<sup>24</sup> This fact has influenced research on the application of these materials for stone conservation.(Cavaletti and Lazzarini 1983, 770) The idea of "reversibility" as generally understood and defined by the *Venice Charter* does not apply to epoxy resins or to thermoplastic resins used in conservation.(Cavaletti and Lazzarini 1983, 770) It is well known now that even if "reversible," these synthetic materials deteriorate over time, thus becoming irreversible interventions on the objects.(Cavaletti and Lazzarini 1983, 770) Further, if badly deteriorated "sugaring" marble, for example, is impregnated with a reversible resin, the consolidation becomes irreversible, since it is impossible to remove the resin without damaging the stone.(Cavaletti and Lazzarini 1983, 770) Lazzarini has recommended a more useful criterion for consolidation products as limited but total reversibility for a few hours after impregnation.(Cavaletti and Lazzarini 1983, 770) This type treatment allows adequate time for necessary operations such as retouching to control the aesthetic effect of the treatment.



The general disadvantages of standard aromatic epoxy resins for their application in this field are:

- ♦ high viscosity and low permeability capabilities for porous structures;
- ♦ low stability to UV radiation that produces a quick and marked yellowing of exposed surfaces;
- ♦ average to low resistance to chemical attack by oxygen and sulfuric acid produced by air pollution. A consequence of this is loss of mechanical properties and detachment of epoxy films from their substrates;
- ♦ a lack of hydrophobic properties that hinders the impregnation of stones with even very slight humidity.(Cavaletti and Lazzarini 1983, 770)

In spite of their negative behavior, however, aromatic epoxies used as adhesives, and consolidants can achieve good results. Various solutions of aliphatic epoxy resins, used in stone conservation, do not exhibit the major disadvantages associated with aromatic resins. These solutions are characterized by:

- ♦ low viscosity at average concentrations, in a range of 10 to 15%;
- ♦ good color stability;
- ♦ strong hydrophobic properties allowing water miscibility;
- ♦ high mechanical strength.(Cavaletti and Lazzarini 1983, 770)

Some important disadvantages of these epoxy resins are low chemical resistance and toxicity due to their water solubility.(Cavaletti and Lazzarini 1983, 770)





### 1.3.2 APPLICATION OF EPOXY RESINS

Epoxy resins for consolidation should be applied as dilute solutions (10-15%) in selected solvents. It has been found that the best results are obtained with mixtures of aromatic hydrocarbons with aliphatic alcohols such as toluene and methanol.<sup>25</sup> After impregnation, washing off superficial resins reduces the risk of discoloration. During cure, the resin polymerizes in the pores of the stone. As the solvents evaporate, only 10-15% of the soluble fraction of the resin migrates to the surface pores.(Ginnel et al. 1994, 7) Total light resistance can be obtained by an additional impregnation with organo-silicones or light resistant thermoplastic resins.(Ginnel et al. 1994, 7)

The change in appearance following treatment with an epoxy formulation is the principal disadvantage to the use of this effective consolidant. The stone surface often darkens and takes on a darker color. Darkening of epoxy resins used in conservation is a common observation. The effect is usually associated with photodegradation of the amine hardener and of the resin. Stone surface darkening occurs when the diffusely scattering, rough stone becomes less rough and more reflective with the application of the epoxy. The two primary solutions to these problems are: (a) the use of amine hardeners and resins that do not react with light and oxygen to form colored degradation products and (b) the reduction of the surface deposition of the cured resin.<sup>26</sup> It is possible to minimize the



deposition of the epoxy resin on the surface of the stone by wiping excess resin immediately after treatment, and wrapping the treated stone in a polyethylene film. This application method increases the resistance of the stone to deterioration, while causing minimal change in the appearance, porosity and permeability of the stone. (Ginnel et al. 1994, 8)



#### 1.4 CHARACTERIZATION OF ALKOXYSILANES USED FOR STONE CONSERVATION

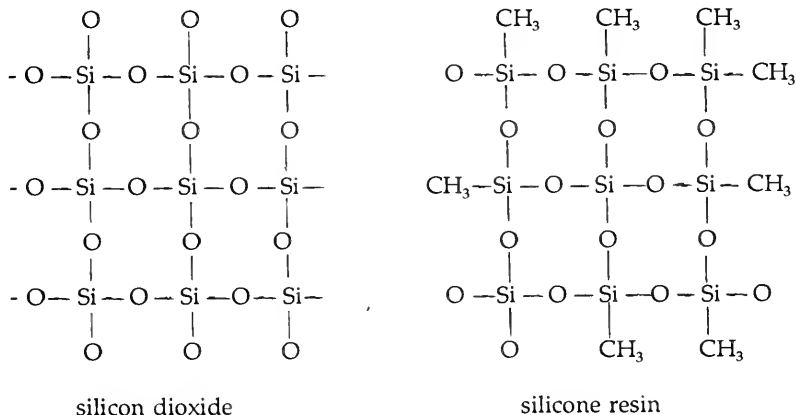
Alkoxysilanes have provided successful results in stone consolidation primarily due to their chemical stability and high depth of penetration. The use of alkoxysilanes for the treatment of deteriorated stone began as early as the 1860s. Extensive laboratory research and field tests carried out in Germany in the 1960s showed that alkoxysilanes can provide good consolidation, while causing minimal damage to the stones.<sup>27</sup> Alkoxysilanes have since been used on deteriorated stones at many historic sites in Germany. Since 1972, ethyl silicate, and mixtures of ethyl silicate and organo-silicon hydrophobic agents have been commercially available in Western Europe, the United States, and Canada.<sup>28</sup> The availability of ethyl silicates and silanes resulted in a rapid increase in interest in the use of tetraethoxilanes and related species such as alkoxysilanes and alkoxysilane-acrylic-polymer mixtures for stone consolidation.

Alkoxysilanes are a group of synthetic organic monomers that can hydrolyze with water to produce either silica or chains of alkylpolysiloxanes. The alkoxysilanes most commonly used as stone consolidants include tetraethoxysilane (ethyl silicate or silicic acid ester), triethoxysilane, and trimethoxymethylsilane. Polymerization of alkoxysilanes takes place in a two-step process, by hydrolysis and condensation. The process results in the formation of siloxane linkages (Si-O-Si) which impart the consolidant its strengthening effect. Several factors control the rate of polycondensation and the structure of the products formed. The major



factors include the amount of water used in the reaction, and the type of catalysts and solvents used. Alkoxysilanes with additional organic groups can also provide water repellency. In addition to forming a binder similar to that of siliceous sandstone, alkoxysilanes can penetrate deeply into porous stone due to their low molecular weight. Their high cost and tendency to darken the color of the stone,<sup>29</sup> and the possible evaporation of the consolidating solution from the surface before hydrolysis<sup>30</sup> are the principle problems associated with their use. Alkoxysilane treatments are also irreversible.

The major advantage of using alkoxysilanes for stone consolidation is attributed to the similarity their chemical structure to silicious minerals. The similarity between alkoxysilanes and silica sand can be observed in the chemical formulas of silicon dioxide and a silicone resin.

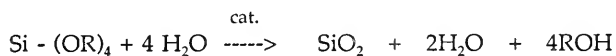


If the silicone resin is applied correctly, the water absorption of the stone may





decrease by 1% or less, while the water vapor permeability may decrease by only 5 to 8%.<sup>31</sup> All silicones are highly UV resistant due to their "SiO<sub>2</sub>-like" structure. Two types of silicone esters developed in Germany for stone consolidation are available commercially as derivatives of silicone esters in special solvents. Wacker Chemie's Stone Strengthener H system has water-repellent additives while the Stone Strengthener OH system is a simple silicone ester-solvent mixture. Both systems react according to the following chemical equation:



In each reaction, a silic dioxide group is formed and a water a hydroxide group released.

Ethyl silicates have been used extensively in Europe on sandstones at historic sites. The general formula for the alkoxysilane is RSi (OR')<sub>3</sub> and for silicic acid ester Si (OR)<sup>4</sup>. Both polymerize by hydrolysis followed by condensation, with the evolution of an alcohol, and formation of polymers based on a silica (SiO<sub>2</sub>) lattice. Both systems consolidate the stone by coating the surface of the pores. Ethyl silicate consolidants are commercially available as a one-pack system containing a diluent and a catalyst. Ethyl silicates improve the physical strength of stones, but can prevent the removal of dirt after consolidation. Due to their chemical nature, ethyl silicates impart no water repellency. Ethyl silicates also cause minimal change in the vapor permeability and water evaporation rate of



stones. The binding action of the silica through the hydrolysis of the ethyl silicate can increase the mechanical strength of stone considerably.

### 2.3.1 CHEMISTRY OF ALKOXYSILANES

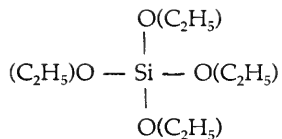
Alkoxysilanes are silanes containing at least one alkoxy group. A silane is a compound based on a silicon chain. Alkyl groups and/or alkoxy groups attach to this chain through a silicon-carbon link (Si-C, silane link) or an ester link (Si-O-C). Some silanes, such as triethoxymethylsilane and trimethoxymethylsilane, contain both silane and ester links.

The alkyl group is a hydrocarbon that occurs in alkoxysilanes in various forms. Alkyl groups such as methyl ( $-\text{CH}_3$ ) or ethyl ( $-\text{C}_2\text{H}_5$ ) group occur in many alkoxysilanes used for stone conservation.<sup>32</sup> These hydrocarbon groups are often represented by the letter R. These alkyl groups can bond with oxygen atoms and form alkoxy groups, such as methoxy ( $-\text{OCH}_3$ ) and ethoxy ( $-\text{OC}_2\text{H}_5$ ).

#### 1. Ethyl Silicate (Tetraethoxysilane) [ $\text{Si}(\text{OC}_2\text{H}_5)_4$ ]:

Ethyl silicate is the alkoxysilane most commonly applied in stone conservation. Ethyl silicates may also be referred to as tetraethoxysilanes, silicic acid esters, silicon esters, and tetra(ethyl)orthosilicates (TEOS). The chemical structure of ethyl silicates may be represented as follows:

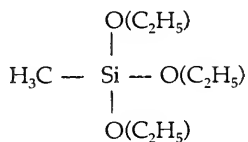




Ethyl silicates have very low viscosity (0.6 cP at 20°C),(Grissom and Weiss, 152) lower than that of water (1.0 cP at 20°C).<sup>33</sup> This property provides ethyl silicates with the ability to achieve deep penetration in porous materials. To achieve deep penetration, however, it is usually necessary to apply large quantities of the material.<sup>34</sup> Ethyl silicate is also highly volatile. It is therefore necessary to monitor and control the application conditions to prevent evaporation of the solution during the hydrolysis and condensation of the solution.<sup>35</sup>

## 2. Triethoxymethylsilane [(CH<sub>3</sub>) Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]:

This compound is chemically similar to ethyl silicate, except for the substitution of an ethoxy group by a methyl group. In studies for stone conservation, this compound is usually referred to as methyltriethoxysilane (MTEOS). The chemical structure of this compound may be represented as:

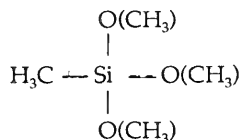




The viscosity of triethoxysilane (0.6 cP at 20°C) is lower than that of water (1.0cP at 20°C).<sup>36</sup> In addition to their ability to consolidate porous materials, due to the exposed methyl groups in the cured product, triethoxymethoxysilanes can to provide water repellency.

### 3. Trimethoxymethylsilane [ (CH<sub>3</sub>) Si (OCH<sub>3</sub>)<sub>3</sub>]:

Trimethoxymethylsilane is structurally similar to triethoxymethylsilane, except for the substitution of the ethoxy groups by methoxy groups. In many scientific studies for stone conservation, this silane is referred to as methyltrimethoxysilane (MTMOS). The chemical structure of this compound may be represented as:



Trimethoxysilanes are low viscosity monomers (0.5 cP at 20°C)(Ashley-Smith and Wilkes, 125) and have the ability to provide consolidation and water repellency to porous materials. The high toxicity of trimethoxymethylsilanes however presents a major disadvantage to their application in the field.<sup>37</sup> Triethoxymethylsilanes and trimethoxymethylsilanes are often referred to as methyl(trialkoxo)silanes or, more generally, alkyl(trialkoxo)silanes. They are usually more expensive than ethyl silicate.





#### 1.4.2 POLYMERIZATION OF ALKOXYSILANES: HYDROLYSIS AND CONDENSATION

Alkoxysilanes are characterized by the hydrogen-silicon connection. The hydrogen stabilizes the silicon bond, while the silicon-oxygen bond has hydrolytic properties. Through hydrolysis, alkoxysilanes generate a hydrate silicone network that consolidates the stone. The resulting product has two hydrolytic groups which can generate a chain product. When the product is deposited, and condenses in the stone, the  $\text{CH}_3$  group, a neutral molecule with no affinity for capillary walls or with water, reacts with other  $\text{CH}_3$  groups, and generates a chain whose structure connects with the  $\text{Si-OH}$  molecule. The non-polar parts ( $\text{CH}_3$ ) push away (i.e., repulse) the polar part of the molecule, and begin to face outward, creating a barrier with no affinity to water. The presence of these non-polar groups in the structure of the stone imparts hydrorepellent properties to the stone. Some silane products can act both as consolidants and as water repellents. Ethyl silicates only provide consolidation, and are therefore recommended for homogeneous materials with low vapor permeability (e.g., bricks), but can also provide good consolidation for porous materials such as sandstones and tuff. It is possible to apply alkoxysilanes to all types of stones. Silanes may also be used as water repellents on both homogeneous or inhomogeneous stones.<sup>38</sup>

The application of alkoxysilanes for stone consolidation is based on the hydrolysis and condensation of the liquid compound within the stone. As the



liquid alkoxysilane penetrates the stone, the initial liquid component reacts with liquid water or water vapor, and hydrolyzes.<sup>39</sup> The hydrolysis reaction of the monomeric alkoxysilane molecule in the stone results in its polymerization. Hydrolysis is the split reaction of an alkoxysilane with water and/or the hydroxyl groups (-O-H) on the surface of a mineral grain. The alkoxy groups (-O-R) of alkoxysilanes then react with hydroxyl groups. The hydrolysis reaction produces a silanol, and releases alcohol. The alcohol, harmless to the stone, evaporates rapidly from the stone matrix.

Two silanol molecules, produced during the hydrolysis reactions, can react, and condense to form a dimer molecule. Further hydrolysis and condensation may then proceed simultaneously and form trimers, tetramers, and then form, a -Si-O-Si-O-Si- network, called siloxanes. These silicone-oxygen-silicon produce the consolidation and strengthening effect.<sup>40</sup>

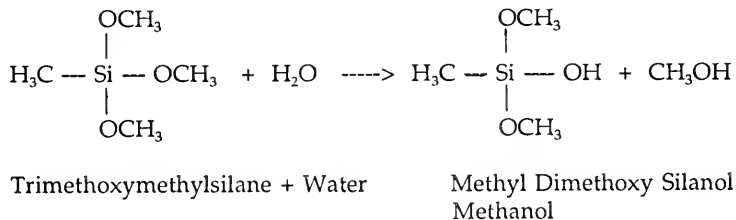
An alkoxysilane is a mobile liquid; as hydrolysis and condensation reactions proceed, the liquid transforms into a glassy solid. The network polymer first forms a soft gel; the gel then shrinks and hardens; the shrinkage continues and the polymer changes into a hard, brittle glass. The polymer finally shrinks into small, glassy polymers or crumbles into a fine powder.<sup>41</sup> If the alkoxy groups react with the hydroxyl groups present on the surface of the stone grains, they bond to the substrate. If the reaction takes place with hydroxyl groups of water molecules, the resulting network of polymers fills the intergranular spaces of the stone. There are conflicting opinions among



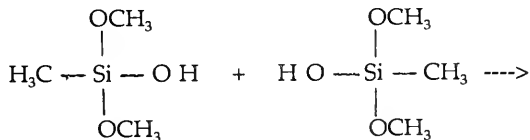
conservators and scientists regarding the importance of the chemical bond in consolidation. According to A. E. Charola, the absence of chemical interaction with the substrate may be an advantage. (Charola, Wheeler and Freund 1984, 180)

When alkoxy silanes with alkyl groups [alkyl(trialkoxy)silanes] polymerize, unlike the Si-O-C link (ester link), the Si-C link (silane link) resists hydrolysis; the product retains alkyl groups attached to the siloxane chain. The alkyl groups present a non-polar aspect to surrounding molecules, and provides water repellency. For example, trimethoxysilane is polymerized as follows:

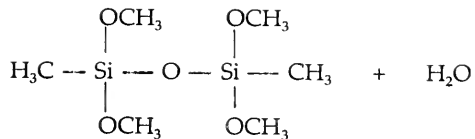
1. The methoxy groups are hydrolyzed to form a silanol, and methanol is liberated:



2. Two methyl dimethoxy silanol molecules react and condensation takes place. Silicon-oxygen-silicon bonds are then formed and water is released:

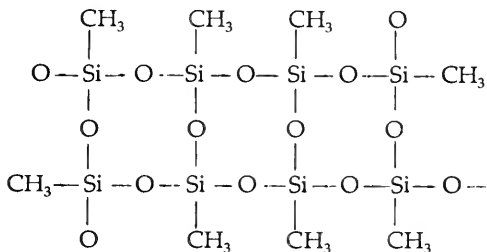






During the polymerization process, water is both produced and consumed.

3. Further hydrolysis and condensation reactions convert -Si-O-C linkages into -Si-O-Si- linkages and generate a three-dimensional cross-linked polymer similar to silica:



The methyl groups are left exposed; this provides water repellency to the polymer compound.

The polymerization of cross-linked polymers requires the presence of certain conditions. These conditions are:





♦ Presence of water: the partial reaction of the alkoxysilane liquid with water initiates polymerization. The presence of a sufficient amount of water is critical in the initial solution to produce gelation. Neither the hygroscopic moisture content of the masonry materials itself, nor the atmospheric humidity, however, can provide sufficient water for polymerization.<sup>42</sup> The amount of water used in the reaction therefore has a direct impact on the mechanism of gel formation.

♦ Solvents: It is necessary to use a solvent in the starting solution to induce the solubility of the water in the alkoxysilane. Ethyl alcohol is usually used as the mutual solvent to induce the miscibility of ethyl silicate and water.(Grissom and Weiss, 152) Methanol and cellusolve are two solvents used with methyl (trialkoxo) silanes (MTEOS, MTMOS)/ water mixture.(Grissom and Weiss, 153) The addition of solvents to alkoxysilanes also reduces their viscosity.<sup>43</sup> Increasing the viscosity of the silanes can assist in controlling the depth of penetration.

♦ Catalysts: Catalysts are used to accelerate the rate of hydrolysis and condensation reactions, and prevent the evaporation of the monomer before polymerization. It is necessary to use catalysts to increase the polymerization rate in field conditions. Acids, especially hydrochloric acid and phosphoric acid, alkalis and metallic salts are used as catalysts for both hydrolysis and condensation.<sup>44</sup> The choice of solvents and catalysts is critical in achieving good



consolidation. In selecting a solvent and catalyst to increase the rate of polymerization, it is necessary to ensure that neither the solvent nor the catalyst reacts with the substrate and leave any soluble residue that can cause further deterioration.

The polymerization rate has a critical impact on the structure and quality of the product formed. Penetration of the monomer liquid into the stone requires considerable time, varying from several hours to one day.(Öztürk 1992, 57) If the liquid has high volatility, however, it can evaporate before adequate penetration. If polymerization occurs too rapidly, gelation can occur before effective penetration, and consolidation only occurs on the surface. Adjusting and controlling the rate of polymerization is one of the most complex problems in stone conservation. Besides the use of catalysts and solvents, several other factors such as the type of hydrocarbon group (methyl, ethyl, etc.) attached to the silane molecule and the relative humidity at which the reaction takes place influence the polymerization rate.(Öztürk 1992, 58)

An experiment on uncatalyzed polymerization of trimethoxymethyl silane, carried out by A. E. Charola, revealed that the relative humidity (RH) has a direct effect on polymerization rate and the quality of the polymer.<sup>45</sup> This study found that the relative humidity must reach a range between 50% and 30% for the application of trimethoxymethyl silane.<sup>46</sup> Above 50%, hydrolysis occurs too rapidly, and during condensation, and stresses can develop, leading to cracks and defects. Below 30%, the reaction takes place too slowly, and allows excessive



evaporation of silane. It is extremely difficult to control relative humidity in the field, however. Even if the environment has an ideal relative humidity, the moisture content of the stones usually vary at different depths. Variability in environmental conditions has a direct effect on the rate and extent of polymerization.

In addition to providing appropriate conditions for polymerization, it is important to characterize the physical properties of the stone. The chemical and physical nature of the substrate has a direct influences the polymerization process. Alkoxysilanes react differently with different types of stones. The presence of -OH groups in the substrate, for example, can lead to the attachment of siloxane chains to the mineral grains. Alkoxysilanes therefore react well with porous, fine-grained stones with surface hydroxyl groups, such as clay-rich sandstones, and bricks.



### 2.3.3 APPLICATION OF ALKOXYSILANES

Alkoxysilanes are usually either sprayed or brushed onto the stone substrate in repeated applications referred to as "cycles." The number of applications and the interval between applications or cycles varies for different products. Each product must be applied according to the manufacturer's recommendations. The stone usually absorbs the resin very poorly in the initial stages. The application of the resin continues until the stone reaches saturation. If necessary, absorbent tissue placed below the treatment area will prevent the polymerization of excess silane on the surface of the stone. Adjacent areas, not designated for treatment, must be protected with sheets of polyethylene film fixed firmly against these surfaces, or by other protective materials such as adhesive tapes, or non-oily modeling clay.(Öztürk 1992, 59) After application of the consolidant, excess resin must be washed off the surface immediately with a cleaning solvent (e.g., methyl ethyl ketone) to prevent surface discoloration.





## CHAPTER TWO

### EXPERIMENTAL PROGRAM

#### 3.1 OVERVIEW

An experimental program was designed for the conservation of the volcanic tuff blocks at the Old Stone Church of Mission San Juan Capistrano, California.(Fig.1) The structure was completed in 1806, and functioned as the church of the mission and local community until its destruction six years later, in 1812 by an earthquake which destroyed the bell-tower, and the three domes over the nave. In the 1860s, local enthusiasts initiated restoration efforts at the church, and reconstructed the walls of the nave with adobe bricks. In an attempt to remove debris from inside the church with dynamite, the group accidentally destroyed the three domes over the transept. The collapse of the domes over the transept further exposed the masonry materials in the nave and transept. Since the 1860s, the transept and nave of the church have remained exposed to the weather. In 1991, scaffolding and water-sheds were erected for seismic stabilization, and to provide the walls a measure of protection from the rain.(Figs.2-3)

The continuous action of rain, wind and sunlight has led to the severe deterioration of the stones and plasters on the interior of the church. The volcanic tuff blocks used in the cornices, pilasters and decorative details in particular have



deteriorated significantly. The stones show signs of disaggregation, microcracking, deep cracking, flaking and loss. The yellow sandstone used in the arches in the nave of the church also exhibit signs of disaggregation, cracking, and surface loss. The green sandstones at the base of the walls exhibit flaking, contour scaling, subfluorescence, and efflorescence.

A conditions survey of the stones on the interior of the church, conducted in December 1993, identified the most significant deterioration mechanisms present on the interior of the Old Stone Church. The volcanic tuff blocks were identified as the stones in most immediate need of conservation intervention. Water penetration, and internal stresses caused by continuous wet-dry cycles presents the main cause of deterioration of these stones. An experimental program was therefore designed to characterize the tuff, as well as the other stones present at the church, to define and classify the major deterioration mechanisms present, and to test possible materials and methods for the conservation of the volcanic tuff blocks. The experimental program assessed the performance of an epoxy resin and ethyl silicate as consolidants, and an epoxy resin adhesive for repairing the cracks in the stones. The test results showed that both consolidants impart satisfactory grain-to-grain cohesion and increase the strength of the stones, causing little change in the permeability, porosity and appearance of the stones, and that injection of the adhesive repaired the cracks, and increased the resistance of the stones to water penetration.

The second part of the experimental program will involve the application



of the same materials on a representative area at the Old Stone Church, and their evaluation after one year. The most successful system will then be selected for use in a comprehensive conservation program for the volcanic tuff blocks on the interior of the church. The masonry conservation program, however, will require cyclical monitoring to survey the site for the reoccurrence of deterioration, and to guarantee timely conservation interventions.



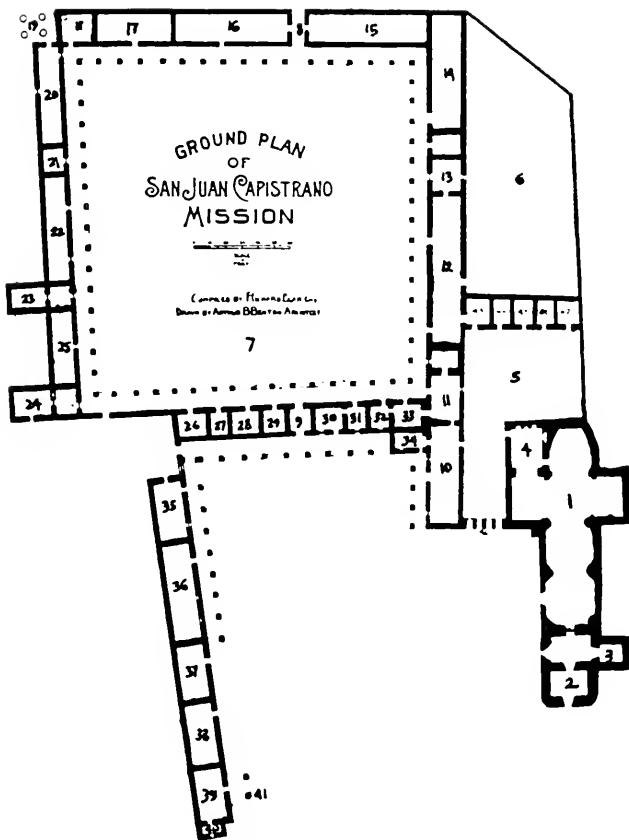


Fig. 1. Plan of Mission San Juan Capistrano, in San Juan Capistrano, California. The Old Stone Church, built in 1806, and destroyed in an earthquake in 1812, now stands as a ruin. The Serra Chapel (2), built in 1776, is now the current chapel of the Mission and local community (Z. Engelhardt 1922, 9).





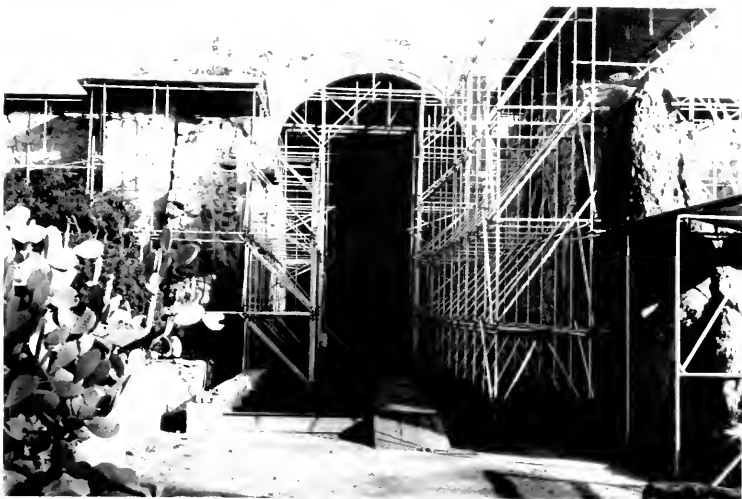


Fig. 2. View of nave of Old Stone Church, Mission San Juan Capistrano (1994).

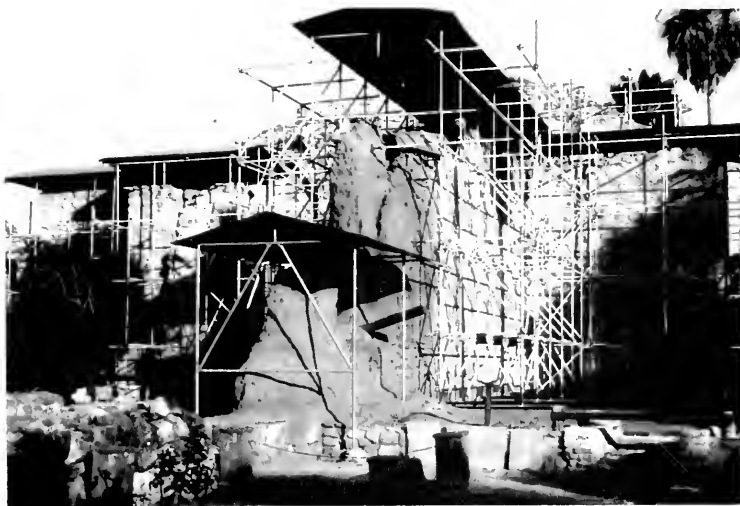


Fig. 3. View of exterior wall of nave and east transept of Old Stone Church (1994).



### 3.2 CHARACTERIZATION OF STONES

The primary structural material used at the Old Stone Church is stone. Several types of stone were used at the church, due to their availability and physical properties (i.e., appearance, strength, ease in carving). Analysis of hand specimens, and petrographic analysis of thin sections identified three major types of stone on the exterior and interior walls of the church: a gray, volcanic tuff, a green, loosely compacted siliceous sandstone, and a yellow, densely compacted siliceous sandstone. The soft volcanic tuff occurs primarily in the carved decorative cornices, pilasters, arches and door frames on the interior of the church, probably because of its ease in carving. The densely compacted yellow sandstone occurs in the interior and exterior walls, arches, doorframes and decorative features, and as structural material.(Fig.4) The loosely compacted green sandstone occurs on the exterior and interior walls, primarily as structural material. Bricks were used as structural material on in the arches and transept walls on the interior of the church. (Fig.5) The function and conditions of these stones are described in detail in Chapter 4.

The green and yellow sandstones, used both in the exterior and interior walls, and the arches on either side of the nave and pilasters on the interior of the church, exhibit flaking, exfoliation, and contour scaling. Although relatively easy to carve, these densely compacted stones have resisted deterioration quite well. The volcanic tuff blocks, used in the cornices, pilasters, arches and decorative



details throughout the interior of the church, have deteriorated very badly. The irregular compaction and weak structure of the tuff has allowed water to penetrate and create internal stresses within the stone. The continuous action of water, and wet-dry cycling, and the penetration of soluble salts from adjacent mortars, and their crystallization in the micro-structure has resulted in severe disaggregation, and cracking.

Petrographic analysis of thin sections of the stones identified the mineralogical composition, and geo-physical structure of the three major types of stones as follows:

### 1. Volcanic tuff:

<b>crystallinity:</b>	holocrystalline
<b>texture:</b>	parallel bedding of crystals in some areas
<b>grain size:</b>	small to medium
<b>mineralogy:</b>	
1-5%	biotite (texture striated)
1-3%	olivine (small crystals with conchoidal fracture)
1-5%	alkali feldspar $An_{65-80} Ab_{20-40}$
35%	quartz
2%	vesicular quartz
<b>stone matrix:</b>	ash and alkali feldspar matrix

### 2. Yellow sandstone:

<b>crystallinity:</b>	holocrystalline
<b>texture:</b>	equigranular texture, high compaction
<b>grain size:</b>	small



**mineralogy:**

1%	olivine
2%	alkali feldspar $An_{65-80} Ab_{20-35}$
2%	biotite
65%	quartz

**stone matrix:** quartz and alkali feldspar

**3. Green sandstone:**

<b>crystallinity:</b>	holocrystalline
<b>texture:</b>	equigranular texture, medium to high compaction
<b>grain size:</b>	small to medium

**mineralogy:**

1-5%	alkali feldspar $An_{65-80} Ab_{20-35}$
2%	olivine
2%	biotite
50%	quartz

**stone matrix:** quartz and alkali feldspar

Petrographic analysis of the three types of stones also provides considerable information on their diagenesis. The volcanic tuff, composed of minerals formed at relatively low temperatures, suggest that the minerals in this stone formed at the final stages of magma cooling, and subsequently compacted in an ash matrix (Figs. 7-8). The minerals are well-defined, which suggests that the rock has undergone minimal alteration following the compaction of the minerals in the ash matrix. The yellow sandstone, much more densely compacted than the green sandstone, is composed of irregular shaped minerals formed at the later stages of magma cooling (Figs. 9-10). The minerals, densely compacted in the siliceous





matrix, suggests that this stone has undergone several stages of erosion and compaction in its diagenesis. The green sandstone is composed of minerals formed at the later stages of magma cooling, with a high percentage of quartz (Figs. 11-12). Crystals with clear cleavage planes compacted in the ash matrix, suggest that this stone has not undergone much alteration in the compaction of the minerals in the cement matrix.

Analysis of thin sections of the volcanic tuff reveals a preferred direction of compaction of minerals within the ash matrix, and distinct irregularities in the compaction patterns. The euhedral form of the minerals within the ash matrix suggests that the rock underwent minimal changes after the compaction of the minerals in the ash matrix. The loose and irregular compaction of minerals in the porous matrix of the stone therefore allows the penetration and movement of water and soluble salts within these stones. Internal stresses caused by continuous wet-dry cycles, and salt crystallization represents the primary cause of deterioration of these stones. Any treatment of the stone therefore must increase its mechanical strength, and resistance to internal stresses, and decrease water penetration, while maintaining the water vapor permeability. The repair of the cracking in the tuff, on the other hand, requires the application of an adhesive that reduces water penetration, provides structural stability and reintegrates the cracked fragments with the core of the stone.





Fig. 4. View of east wall of nave, Old Stone Church (1994). The load-bearing stones are green and yellow sandstone. The stones in the cornice and pilaster are volcanic tuff, and the stones in the arch yellow sandstone and tuff. Fragments of lime-based plaster are present below the cornice and arch.





Fig. 5. West wall of nave, Old Stone Church (1994). The load bearing stones are yellow and green sandstone. The core of the wall consists of rubble stone, brick, and lime-based mortar.



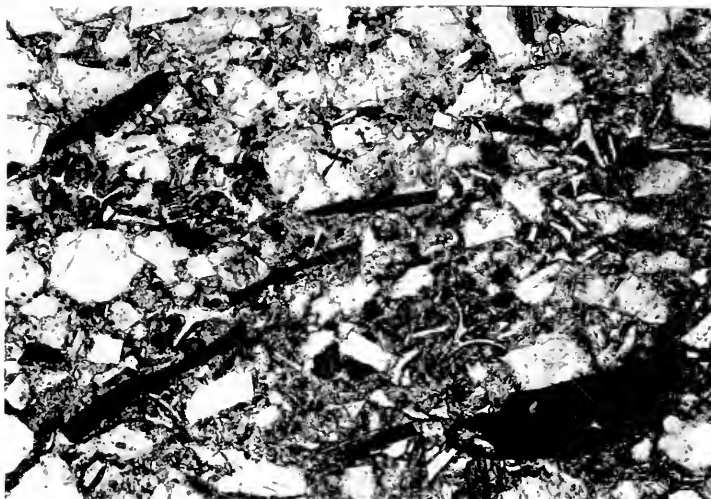


Fig. 6. Thin section of volcanic tuff (  $\times 12.5$  mag, normal light).

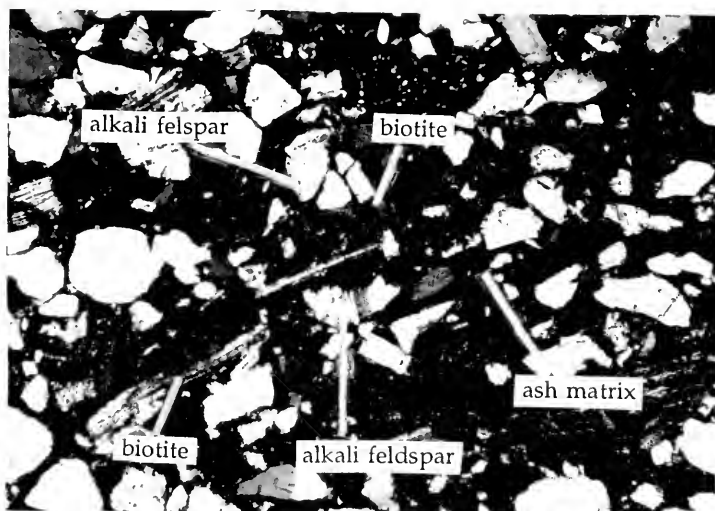


Fig. 7. Thin section of volcanic tuff (  $\times 12.5$  mag, at crossed polars).







Fig. 8. Thin section of yellow sandstone (  $\times 12.5$  mag., normal light).

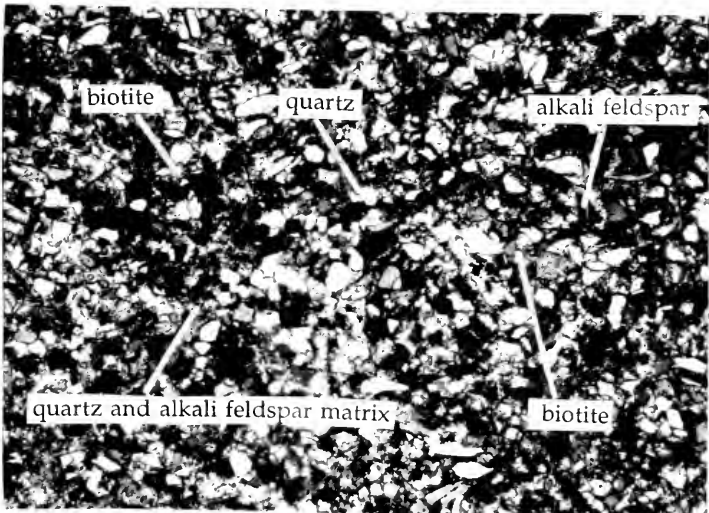


Fig. 9. Thin section of yellow sandstone (  $\times 12.5$  mag. at crossed polars).



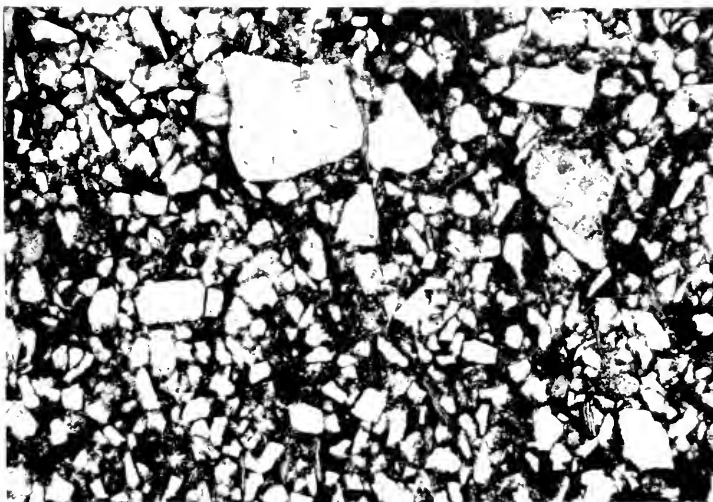


Fig. 10. Thin section of green sandstone (  $\times 12.5$  mag., normal light).

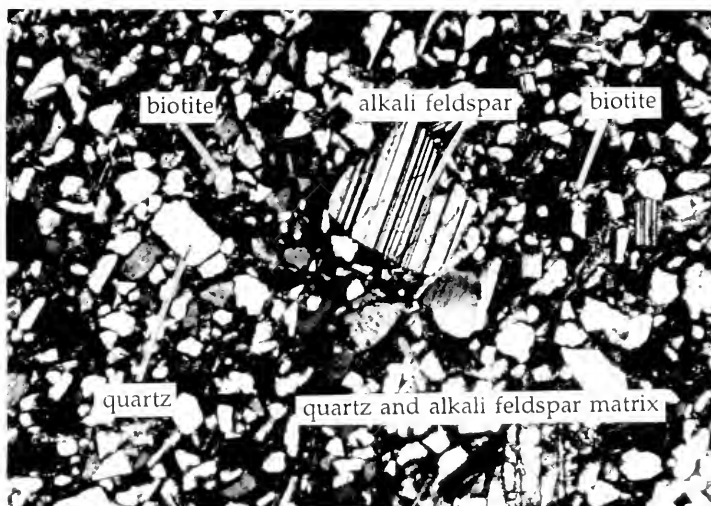


Fig. 11. Thin section of green sandstone (  $\times 12.5$  mag. at crossed polars).



### 3.3 CONDITIONS OF TUFF BLOCKS

The existing conditions of the tuff blocks used in the cornices, pilasters, and decorative details on the interior of the Old Stone Church vary widely from block to block. The variability in the conditions of the stones is attributed to the mineralogical and physical properties of the stones, as well as their orientation, and location in the building, and exposure to different microclimates and weather conditions. The mineralogical composition and physical properties of the stones, the preferred direction of compaction of the minerals in the cementing matrix, the composition of the cement matrix, the direction of bedding planes, and the orientation of the stones in the building all influence the causes, extent and rate of deterioration of the stones. Variations in temperature, exposure to sunlight, rain, wind all influence the condition and rate of deterioration of each block.

The tuff blocks, laid either parallel, horizontal or diagonal to the surface of the wall, exhibit considerable variability in their macrostructure and present conditions. The compaction patterns vary from irregular patterns to a preferred direction of compaction and distinct bedding planes. The present conditions of these stones range from disaggregation, severe cracking, flaking, contour scaling, surface losses and surface erosion. The width of the cracks in the stones range from > 1 mm. to 10 cm. and the depth of the cracks from > 1 mm. to 20 cm. In addition to the mineralogical composition and physical characteristics of the stones, their exposure to the weather in varying degrees (i.e., temperature,



sunlight, shade, rain) contribute to the variability in their conditions. The existing conditions of the stones are discussed in further detail in Chapter 4.

### 3.4 SELECTION OF TREATMENTS

The selection of treatments for the volcanic tuff began with research on previous studies on the consolidation and mechanical repair of porous stone. The consolidation systems were selected based on their ability to impart mechanical strength and grain-to-grain cohesion, and to decrease water penetration while maintaining the water vapor permeability of the stone. The adhesive was selected based on its ability to impart structural reintegration and gap-filling, and decrease water penetration without damaging the stone. The following two products were selected for consolidation: (1) OH Stone Strengtheners, Conservare (Prosoco, Inc.) an ethyl silicate, and (2) Eponex 1510 (Shell Chemical), an aliphatic epoxy resin used as a 10% solution in toluene and isopropanol. Both ethyl silicate and epoxy resin have the ability to increase grain-to-grain cohesion and mechanical strength while maintaining water vapor permeability, and causing minimal discoloration. Both ethyl silicate and epoxy resin have low viscosity and the ability to achieve high depth of penetration. Epon 828, manufactured by Shell, selected as an adhesive, has low viscosity, imparts mechanical strength, and resists discoloration. Ethyl silicates tested extensively for the consolidation of porous stones, usually





provide good results, but some discoloration. The discoloration, however, disappears over time. The treatments were applied in the following formulations:

#### **Step I- Consolidation**

- (1) OH Stone Strengthener, Conservare (Prosoco, Inc.) ethyl silicate, undiluted; cure time: 2-3 weeks;
- (2) 10 parts Eponex 1510 (Shell Chemical), cycloaliphatic resin (hydrogenated bisphenol-A epichlorohydrin).  
  
3.5 parts Jeffamine D-230 (Texaco Chemical), a polyoxypropylene diamine hardener in a 10% solution of toluene : isopropanol solvent mixture (1:5); cure time: 2-3 weeks.

#### **Step II- Adhesive injection**

Epon 828 (Shell Chemical), a difunctional bisphenol-A epichlorohydrin derived epoxy resin, and

Jeffamine D-230 (Texaco Chemical) (100 : 32); cure time: 7 days.

The epoxy resin, EPONEX 1510, was applied by partial immersion for 15 minutes, the surface of the specimens wiped with acetone, and wrapped in a polyethylene film for the duration of the cure (i.e., two weeks, at room temperature). The ethyl silicate, CONSERVAR OH, was applied by partial immersion for 2 minutes for three cycles, with a 15 minute interval between each cycle. The surface of the specimens were wiped with methyl ethyl ketone, and cured for two weeks at room temperature. The adhesive resin, EPON 828, modified with 4% w/v Grade-5 Cab-O-Sil amorphous fumed silica, was injected into assemblies of tuff simulating the cracks in the stones with a 16 g ½ needle and syringe and allowed



to cure for two weeks at room temperature.

### 3.4 FORMULATION AND TREATMENT OF FACSIMILES

Stone samples for the experimental testing program, obtained from the site of the Old Stone Church at Mission San Juan Capistrano, were cut into various sizes and shapes for the tests. Deteriorated volcanic tuff blocks found near the base of the interior walls of the church collected during the conditions survey of the church in December, 1993, were transported to the Architectural Conservation Laboratory at the University of Pennsylvania. The standardized physical tests, selected to assess the two consolidants and adhesives and their ability to deter deterioration, require specimens of specific sizes and shapes. The stone specimens, sawed with a "glass" blade (i.e., a blade designed for cutting soft stones) into cubes and slabs of the appropriate size and shape, were cut into the following sizes:

Test Name	No. Specimens	Specimen size
Modulus of Rupture (ASTM C99-87)	9	(2 x 4 x 8) cm.
Compressive strength (ASTM C170-97)	12	(4 x 4 x 4) cm.
Absorption and bulk specific gravity (ASTM C97-83)	9	(4 x 4 x 4) cm.



Water vapor transmission (ASTM E96-80)	12	(3 x 1.25) cm.
Depth of penetration (Iodine Vapor)	6	(4 x 4 x 2) cm.
Accelerated weathering test (QUV/SE/SO)	6	(5 x 4 x.5) cm.
Shear Strength (ASTM D905-89)	12	2 (3.5 x 7x1.5)cm.

The specimens, cut in similar directions, parallel or perpendicular to the preferred direction of compaction, for each test, ensured uniform conditions for the tests. The sizes of some of these samples were reduced by a small fraction during their preparation. It is necessary for all specimens to have smooth surfaces and opposite sides absolutely parallel to minimize the margin of error in the tests. Three sets of specimens were prepared for each test: (1) samples consolidated with epoxy resin, (2) samples consolidated with ethyl silicate, and (3) unconsolidated samples. The first set of samples was consolidated with the epoxy resin solution by partial immersion for 15-20 minutes, wiped with a cloth saturated with acetone, wrapped in a polyethylene film and cured for two weeks. The second set of samples was consolidated with ethyl silicate by partial immersion in three successive cycles, and cured for two weeks. The third set of samples, or "control" samples, was not unconsolidated. The assemblies prepared for the shear strength test were consolidated with both treatments and injected with the epoxy adhesive and cured for one week.



### 3.6 EXPERIMENTAL TESTING PROGRAM

Assessment of the effects of consolidation and adhesive repair of the volcanic tuff requires an profound understanding of the stone's properties both before and after the proposed treatments. To this end, a series of standardized tests was performed on treated and untreated specimens of tuff to examine the physical and mechanical properties of the stone. The tests examined properties such as modulus of rupture, compressive strength, and shear strength, as well as the stone's resistance to deterioration mechanisms connected with the environment such as water vapor transmission, and resistance to salt crystallization, ultraviolet light, and water condensation.

The following standardized tests were selected and modified to suit the purposes of the materials and products examined:

ASTM C99-97 -	"Standard Test Method for Modulus of Rupture of Dimension Stone"
ASTM C170-97 -	"Standard Test Method for Compressive Strength of Dimension Stone"
ASTM E96-80 -	"Standard Test Method for Water Vapor Transmission of Materials"
ASTM D90-89 -	"Standard Test Method for Strength Method for Strength Properties of Adhesive Bonds by Compression Loading"
ASTM C97-83-	"Standard Test Method for Absorption and Bulk Specific Gravity of Dimension Stone"
ASTM G53-88-	"Standard Test Method for Accelerated Weathering"





BRE -	"Sodium Sulfate Crystallization Test".
GCI -	"A New Method for Determining the Depth of Penetration of Consolidants Using Iodine Vapor"

The water vapor transmission test, absorption and bulk specific gravity test and sodium sulfate crystallization test were all performed at the Architectural Conservation Laboratory at the University of Pennsylvania. The modulus of rupture, compressive strength and shear strength tests were performed using an Instron Testing Machine at the Laboratory for Research on the Structure of Matter (L.R.S.M.) at the University of Pennsylvania. Qualitative and quantitative analysis of soluble salts was performed by Delare Laboratories (Philadelphia). The procedures for all the tests performed in the experimental program are provided in Appendix B, and the results of the tests in Appendix C.



## 3.7 EVALUATION OF TEST RESULTS

### 3.7.1 MODULUS OF RUPTURE

The modulus of rupture test provides one of the most accurate methods for assessing the consolidation treatment of masonry materials. This test evaluates both the strength of the stone itself, and the grain-to-grain cohesion and strength of the stone with the consolidation treatment. The results of the test provide an indication of the difference in mechanical strength between the unconsolidated and consolidated stone.

The modulus of rupture test was performed on nine specimens of tuff (i.e., three sets of three specimens), two sets consolidated with epoxy resin and ethyl silicate and one unconsolidated set. The results of the test demonstrate that consolidation with epoxy resin causes a 108.5% increase in mechanical strength, and consolidation with ethyl silicate causes a 108.2% increase over the unconsolidated specimens. The results suggest that both consolidants increase the mechanical strength of the stone to a significant degree. The epoxy resin imparts slightly greater strength, however the difference between the strength imparted by the alkoxysilane and epoxy resin is negligible. Increasing the mechanical strength of the tuff with either the ethyl silicate or epoxy resin system will therefore increase the resistance of this material to further deterioration.



A statistical analysis of the results of the modulus of rupture test shows no evidence of a systematic error in the results of this test. The t-test shows that the observed value of  $|t|$  for all specimens is below the critical value ( $t = 4.30$ ) at the 5% level. The F-test indicates the values obtained for the modulus of rupture of each set of specimens show an insignificant difference in precision at the 5% level. Variations in the results obtained for this test are primarily due to the inhomogeneous nature of the stone itself.

### **3.7.2 COMPRESSIVE STRENGTH**

The compressive strength test was performed on twelve specimens of volcanic tuff (i.e., three sets of four specimens), one set consolidated with epoxy, one set consolidated with epoxy resin and one unconsolidated set. The results of this test indicate that the ethyl silicate imparts slightly greater mechanical strength than the epoxy resin. The data obtained in this test, however, also show that the unconsolidated specimens can display greater mechanical strength than the consolidated specimens. The inhomogeneous nature of the stone is the primary cause of variations in the results of the test. The results obtained for the two sets of consolidated specimens bracket a narrow range (i.e. 5927-6100 kPa, or 859-884 psi). This suggests that the epoxy resin and ethyl silicate impart a similar increase of mechanical strength. It is necessary to repeat the test on specimens cut from



the same block of stone with equal dimensions and parallel faces. This test provides more accurate values for the compressive strength of unconsolidated tuff and tuff consolidated with epoxy resin and ethyl silicate.

Although the statistical analysis of the results for each set of specimens show that the results are precise, the results are inaccurate because the values for compressive strength of the unconsolidated samples appears greater than the compressive strength of the unconsolidated samples. The results for the t-test shows the observed value for t for all specimens is below the critical value ( $t = 3.18$ ). The F-test indicates that there is no significant difference between the results for this test at the 5% level. It is necessary to repeat this test on specimens from the same block with equal dimensions and parallel faces to obtain more accurate results. If the tuff specimens are cut in the same direction (i.e., parallel and perpendicular to the preferred direction of compaction), this test can provide accurate information on the compressive strength of the consolidated and unconsolidated tuff.





### 3.7.3 ABSORPTION AND BULK SPECIFIC GRAVITY

The tests for water absorption and bulk specific gravity were performed on nine specimens of tuff (i.e., three sets of three specimens), one set consolidated with epoxy resin, one set consolidated with ethyl silicate and one unconsolidated set. The results of this test indicate that the epoxy resin reduces the water absorption of the tuff by 1.32% and ethyl silicate by 4.06%. The specific gravity of the tuff increases by 1% if consolidated with epoxy resin, and by 3% if consolidated with ethyl silicate.

The test for water absorption indicates that the tuff maintains its permeability and absorptive properties when consolidated with epoxy resin. Ethyl silicate, on the other hand, causes a slight decrease in both the permeability and absorptive properties of the stone. The test results of the test for bulk specific gravity show that consolidation with epoxy resin causes a minimal increase in the density of the stone. Consolidation with ethyl silicate causes a decrease in absorptive properties, and an increase in density. The results of both these tests however show that consolidation of the tuff with both epoxy resin and ethyl silicate causes a minimal decrease in the water absorption and density of the stone.

The weight percentage absorption of the stone corresponds to the open porosity of the stone. The results of this test therefore provide reasonably



accurate values for the porosity of the tuff. Specimens consolidated with epoxy resin have approximately 18.2% porosity, specimens consolidated with ethyl silicate have approximately 15.4% open porosity and the untreated specimens have approximately 22.7% open porosity. The epoxy resin, in other words, reduces the open porosity of the tuff by 4.5% and the ethyl silicate by 7.3%. The porosity of the tuff specimens consolidated with epoxy resin is therefore more like the original porosity of the volcanic tuff.

A statistical analysis of the results of this test indicate that the values are acceptable. The observed value for  $|t|$  for each set of specimens is below the critical value for  $t$  ( $t = 4.30$ ). The F-test, on the other hand, shows that there is a significant difference in the values obtained for the water absorption of unconsolidated specimens at the 5% level. The Q-test on the suspect value, however, shows that these results are acceptable. The results for these tests are therefore both precise and accurate.



### 3.7.4 WATER VAPOR TRANSMISSION

The results of the water vapor transmission test indicate the water vapor transmission of both the unconsolidated specimens and specimens consolidated with epoxy resin and ethyl silicate are very similar. Neither the epoxy resin, nor the ethyl silicate reduces the water vapor permeability of the original sample of tuff to any significant degree. The results of the test show that the specimens consolidated with epoxy resin have a somewhat lower rate of water vapor transmission ( $WVT = 0.007 \text{ g/t}$ ) than those specimens consolidated with ethyl silicate ( $WVT = 0.008 \text{ g/t}$ ). The rate of water vapor transmission of specimens consolidated with ethyl silicate is very close the water vapor transmission of the unconsolidated specimens ( $WVT = 0.008\text{-}0.01 \text{ g/t}$ ). The statistical analysis of the results for this test indicate that the results are both precise and accurate at the 5% level. These values for the water vapor transmission of consolidated specimens, however, are not accurate enough for the purposes of this test. It is necessary to obtain more sensitive measurements of the water vapor permeability of consolidated and unconsolidated tuff. Application methods must also be tested (i.e., brush, spray, wicking) in the laboratory and/or on site to determine, and evaluate the depth of penetration achieved by each method.



### **3.7.5 DEPTH OF PENETRATION**

The results of the depth of penetration test indicate that both the epoxy resin and ethyl silicate penetrate the tuff to a depth of about 1 cm. The specimens were consolidated with epoxy resin by partial immersion for 10-15 minutes, and with ethyl silicate in three successive cycles of three minutes by partial immersion. Although the ethyl silicate ( $x = 0.88$  cm.) penetrates the specimens further than the epoxy resin ( $x = 0.75$  cm.), the depth of penetration achieved by both consolidants appears satisfactory. A depth of penetration of 1 cm. is acceptable for the consolidation of the tuff. Both consolidants achieve satisfactory penetration.

### **3.7.6 ACCELERATED WEATHERING**

The results of the accelerated weathering test indicate that the unconsolidated specimens remain very similar in color after exposure to UV-B ultraviolet light and consolidation cycles (four three hour cycles of each every 24 hours for two weeks), the specimens consolidated with epoxy resin discolor to light gray, and the specimens consolidated with ethyl silicate discolor to a value darker than light gray. The Munsell Color Chart provides an accurate means of evaluating the color change in the tuff. The unconsolidated specimens remain





approximately the same color, light gray (Munsell 2.5 Y, N 7.5/0); specimens consolidated with epoxy resin discolor to light gray (Munsell 2.5 Y, N 7/0); specimens consolidated with ethyl silicate discolor to a darker light gray (Munsell 2.5 Y, N 6.5/0). Although these values for the color change in the tuff indicate certain range for the color change of samples consolidated with epoxy resin and ethyl silicate, a more accurate method is necessary for measuring the color change.

The most accurate method for measurement of changes in color can be measured using a Minolta, Model CM 1000, chromameter. The chromameter can determine the CIELAB color coordinates ( $L^*$ ,  $a^*$ ,  $b^*$ ), and the E delta values of the specimens. The E delta values represent a standardized means of describing the appearance materials. It is possible to measure the changes in the appearance of the specimens subjected to the accelerated weathering test more accurately using the Minolta chromameter. The chromameter provides an very precise and accurate means for measuring and assessing the light resistance of tuff samples consolidated with ethyl silicate and epoxy resin after accelerated weathering.



### 3.7.7 SODIUM SULFATE CRYSTALLIZATION

The sodium sulfate crystallization test provides a comparative method for evaluating the resistance of masonry materials to continuous wet-dry cycles and salt crystallization. The results of this test show that each set of specimens reacts to water containing 16% solution of sodium sulfate at different rates. The sodium sulfate crystallizes very rapidly in specimens consolidated with epoxy resin (+2.1%, +3.8%), very slowly in specimens consolidated with ethyl silicate (0%, +0.8%), and at a moderate rate in unconsolidated specimens (+ 1.2%, +2.8%). The salt crystallizes rapidly in specimens consolidated with epoxy resin because the salts interact with the epoxy; the salt crystallizes more slowly in the specimens consolidated with ethyl silicate because alkoxysilanes impart a degree of water repellency, and decrease the penetration of soluble salts. These results suggest that consolidation with ethyl silicate reduces the rate of salt crystallization, while consolidation with epoxy resin increases the rate of crystallization. If salt crystallization is a significant cause of deterioration, consolidation with ethyl silicate should provide the stone resistance to the crystallization of soluble salts in the stone matrix. In areas where the penetration of soluble salts and salt crystallization appears to be present a, significant cause of deterioration, consolidation of the tuff with epoxy resin must be avoided to minimize the effects of salt crystallization in the deterioration of the volcanic tuff.



### 3.7.8 SHEAR STRENGTH

The shear strength test was performed on twelve assemblies of volcanic tuff. The specimen assemblies consisted of two square slabs of tuff of equal size separated by two narrow wooden spacers forming an open joint between the two pieces of tuff approximately 0.02" in width. The assemblies were designed to test injectable, gap-filling adhesives to treat microcracking observed in the volcanic tuff blocks. The specimens consisted of three sets of assemblies: one set pre-consolidated with epoxy resin, one set pre-consolidated with ethyl silicate, and one unconsolidated set. After consolidation, all three sets were injected with the selected epoxy adhesive, EPON 828, modified with 4% (w/v) Grade-5 Cab-O-Sil amorphous fume silica. The results of the test show that the assemblies consolidated with epoxy resin and treated with epoxy adhesive have a mean shear strength of 175 psi, and the assemblies consolidated with ethyl silicate and injected with the epoxy adhesive have a mean shear strength of 182 psi. The values of these results suggests that there is no significant difference between the shear strength of assemblies consolidated with epoxy resin or ethyl silicate, and injected with the modified epoxy resin.

A statistical analysis of the results of the shear test shows that there is no significant difference between the precision of the values within each set of samples at the 5% level. The values obtained for the shear strength of these assemblies provide an accurate indication of the shear strength of the treated tuff.



### 3.7.9 QUANTITATIVE ANALYSIS OF SOLUBLE SALTS

The results of the laboratory test for the quantitative analysis for the presence of soluble salts indicate that sulfate and calcium are present in negligible quantities. The penetration of sulfate and calcium salts therefore may represent a minor cause of deterioration. Chlorides, present in very low quantities, can be attributed to the site's maritime location. These salts are present in negligible quantities. Nitrates in the stone can be traced to a variety of sources, including microorganisms present in the stone, or landscape fertilizers. These ions are present in a negligible amount.

Calcium carbonate-containing minerals present in mortars or plasters used in combination with the stone may have deposited the calcium carbonate present in the stone. The calcium carbonate ( $\text{CaCO}_3$ ), almost insoluble, and present in mortars and plasters, will react with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and form soluble calcium bicarbonate, which may then penetrate into the stone matrix. When the stone begins to dry, bicarbonate salts will either recrystallize in the matrix or migrate to the surface of the stone. The presence of these calcium ions represents a possible, but minor factor in the deterioration of the stone.

The sulfates most commonly found in stone are calcium sulfates (gypsum,  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ). These salts may originate from gypsum present in the original plasters adjoining the stone, or atmospheric pollution. Reports on the air pollution for San Juan Capistrano, however, indicate the minimal presence





of atmospheric pollutants in this area.

### 3.8 CONCLUSIONS

The volcanic tuff blocks at the Old Stone Church at Mission San Juan Capistrano in California are in need of immediate consolidation and adhesive repair. Disaggregation, flaking and cracking of the tuff blocks, caused primarily by the penetration of water, aggravating inherent geo-chemical anomalies and the formation of soluble salts, require a consolidation system that will improve the durability of the stone, and increase its resistance to deterioration. In addition, the cracking will require an adhesive that bonds and fills the cracks, minimizing the penetration of water into the stone matrix. The formulation of the consolidant and adhesive resin and application procedures selected for the conservation treatment must cause minimal alteration to the appearance of the stone. The experimental program for the conservation of these tuff blocks provided the initial data for assessing the selected treatments.

The physical and mechanical tests carried out on samples of volcanic tuff from the Old Stone Church show that the epoxy resin solution (Eponex 1510, Shell Chemical, and Jeffamine D-230, Texaco Chemical, in a 10% solution of toluene and isopropanol) penetrates the stone to about 1 cm., increases the modulus of rupture by 9%, decreases the open porosity by 4.5%, and decreases



the water vapor transmission by 12.5%. The ethyl silicate (Conservar OH, ProSoCo) penetrates the stone to about 1 cm., increases the modulus of rupture by 8%, decreases the porosity by 7.3% and decreases the water vapor transmission by a very small fraction below that for the unconsolidated stone. The stone absorbs about 7 g. of epoxy resin per 100 g. of stone (i.e. 7% by weight), and 11 g. of ethyl silicate per 100 g. of stone (i.e. 11% by weight). The epoxy resin penetrates the stone from 0.5 to 1 cm., and the ethyl silicate from .75 to 1 cm.. The accelerated weathering test shows that this epoxy solution causes minimal discoloration in the tuff, changing its appearance from a light gray to a darker light gray. The ethyl silicate causes a slight discoloration of the stone from light gray to a darker gray.

The results of the shear test demonstrate that the assemblies consolidated with ethyl silicate and injected with epoxy resin adhesive (Epon 828, Shell Chemical, and Jeffamine D-230, Texaco Chemical) have a higher mechanical strength than the assemblies consolidated with epoxy resin and injected with epoxy adhesive. The breaks in the stone, however, occur closer to the joint in assemblies consolidated with epoxy resin and further within the stone in assemblies consolidated with ethyl silicate. These results suggest that consolidation of the deteriorated tuff with the epoxy resin and injection of microcracks with the epoxy adhesive would cause less new damage to the stone in the event of stresses (e.g., seismic shock) than consolidation with ethyl silicate and injection of the cracks with epoxy adhesive.



Consolidation of the volcanic tuff with epoxy resin appears to provide the tuff with adequate mechanical strength to delay further deterioration. The epoxy resin also causes minimal discoloration of the stone. Injection of the microcracks with the epoxy resin adhesive readheres and reintegrates the fragments of stone and prevents the rapid penetration of water into the stone matrix. The use of compatible lime-based mortar fills with properties and appearance similar to the tuff to seal the cracks would inhibit the penetration of water and integrate the repaired areas visually with the rest of the stone. This method for the repair of cracking tuff, however, is cumbersome, labor intensive and time consuming. Consolidation with the epoxy resin requires the application of the solution by bulk procedures, by attaching cotton wicking material against the face of the stone and feeding the resin from a container until complete saturation is achieved, wiping the resin remaining on the surface with acetone, and wrapping the stone with polyethylene film for two weeks.

Consolidation of the volcanic tuff with ethyl silicate provides the tuff with mechanical strength and resistance to salt crystallization to delay the deterioration of the stone. The injection of microcracks in tuff consolidated with ethyl silicate, and injection with epoxy resin appears to repair and reintegrate the fragments of stone. These cracks may then be sealed with compatible mortar repairs to minimize water penetration into the crack and to reintegrate the repair with the rest of the stone. The ethyl silicate causes minor discoloration, but previous studies suggest that the stone may return to its original appearance with time.



The ethyl silicate may be applied by brush and allowed to cure for two weeks before the injection of the epoxy adhesive. Consolidation with ethyl silicate provides a relatively easy means to impart the stone greater resistance to deterioration and causes minimal alteration in the stone.

Further laboratory tests must first be applied, however, for more conclusive evidence on how the two consolidation systems interact with the tuff, and alter its physical and chemical properties, to assess the performance of the two systems. The modulus of rupture, compressive strength, and water vapor transmission of tuff consolidated with the two systems must be tested for more accurate measurements. Examination of both systems by scanning electron microscopy will also provide more information on the interaction of the epoxy resin and ethyl silicate within the tuff. It is also necessary to measure the appearance of the consolidated tuff after accelerated weathering with a chromameter to determine their CIELAB coordinates.

Both methods for the consolidation and adhesive repair of the tuff must then be tested on a representative area on site, and reevaluated after at least a year of natural weathering for the selection of the most appropriate method for the conservation of the volcanic tuff blocks. The construction of a test wall with tuff blocks at the site and application of both the epoxy resin and ethyl silicate and injection of the epoxy resin would provide a practical means for evaluating the performance of the two treatments. The deterioration of the test wall may be measured through a mobile grid system at regular intervals for at least one year.





The appearance of the stones may also be measured, and their standard E values determined at regular intervals. The performance of both consolidation systems and the adhesive repair must then be evaluated carefully before selecting an appropriate system for the conservation of the fragile, deteriorated tuff blocks at the Old Stone Church.



### 3.9 RECOMMENDATIONS FOR FUTURE RESEARCH

The results of the experimental program indicate the need for further research in the application of the same treatments both in the laboratory, and the field to assess their long-term performance under field conditions. Both consolidants, EPONEX 1510 and CONSERVAR OH, and the adhesive resin, EPON 828, appear to improve strength and provide resistance to deterioration, while causing minimal change in the porosity, and appearance of the stone. The on-site testing of these materials, however, will require regular monitoring of the test area for at least one year, the removal of core samples for the test area, and reevaluation of their effects on the stones. Due to the deleterious effects of water penetration on these stones, the conservation program should include the application of a water repellent following consolidation, and adhesive repair. The selection of a water repellent will require further laboratory and on-site testing. Each of these tests will require the development and assessment of more sensitive, and precise laboratory tests, and on-site testing.

The laboratory tests must include further tests to determine the physical and chemical properties of the tuff before and after consolidation with EPONEX 1510 and CONSERVAR OH. The laboratory studies must include further examination of the physical properties of the tuff before and after treatment by x-ray diffraction, and scanning electron microscopy (SEM). The physical tests must be applied to tuff specimens from the same block, and cut in the same



direction. These tests must include modulus of rupture and compressive strength tests, and a water vapor transmission test which yield more accurate values for the treated and untreated tuff. The change in the appearance of the core samples of consolidated tuff exposed to the weather must also be measured at regular intervals with a chromameter to determine their CIELAB coordinates. These measurements will provide useful data on the change in the appearance of tuff consolidated with EPONEX 1510 and CONSERVAR OH over time.

Field tests for assessing the performance of the epoxy resin, EPONEX 1510, and the ethyl silicate, CONSERVAR OH, and epoxy resin adhesive, EPON 828 modified with 4% (w/v) Cab-O-Sil amorphous fumed silica, must consist of two components: (1) application of the treatments on a selected field test area, and (2) construction of a mock-up wall of volcanic tuff blocks, and application of the same treatments to selected blocks in the wall. A representative area on the interior of the church, such as the south wall of the west transept, could become the test area for the treatments. The mock-up wall may be constructed with fallen tuff blocks located at the site, or if possible, from the quarry for the volcanic tuff blocks. A movable, metal or plastic grid attached to the outer face of the wall will provide reference points for monitoring the deterioration of the stones at regular intervals. The change in the appearance and rate of deterioration of the tuff blocks in both the test area and mock-up wall may be measured visually or with a chromameter at regular intervals over a one year period.

The conditions survey of the volcanic tuff blocks indicates that the primary



cause of deterioration is the penetration of water into the porous structure of the stone, and internal stresses caused by repeated wet-dry cycles. Both the ethyl silicate and epoxy resin provide mechanical strength to the stone which increases resistance to deterioration, but neither provide water repellency to the stones. A water repellent should be applied to selected areas in the field, and their performance assessed over a one year period. The use of water-repellents on stones reduces the penetration of water without altering the vapor permeability of the stone to a significant degree. An alkoxysilane such as methyltrimethoxysilane (MTMOS) is recommended; these silanes impart water repellency to porous stones without causing significant changes in the appearance or physical properties of the stones.





## CHAPTER THREE

### CASE STUDY: CONSERVATION OF THE VOLCANIC TUFF BLOCKS AT THE OLD STONE CHURCH OF MISSION SAN JUAN CAPISTRANO, SAN JUAN CAPISTRANO, CALIFORNIA

#### 4.1 OVERVIEW

The purpose of this study is the conservation of the volcanic tuff blocks at Old Stone Church of Mission San Juan Capistrano, California. The study began upon the request of the Diocese of Orange County requested for the development of a comprehensive conservation program for the Old Stone Church. The project director for the conservation program was Frank Matero, and the research fellows, Anne Brackin and the author, Evin Erder. This study is the first phase of a multi-phase program that includes the documentation, analysis, and characterization of the original stone masonry, and the evaluation of the results of the experimental programs on conservation treatments. Based on the results of the experimental programs, recommendations have been made for further research on possible methods for the consolidation and repair of the stones, and a program designed to conserve the stones, and delay their deterioration.

The decision to develop a conservation program for the masonry materials at the Old Stone Church at Mission San Juan Capistrano in San Juan Capistrano, California defined the scope of the project. The interior stonework at the Old Stone Church has deteriorated considerably, and requires immediate conservation



treatment to deter further deterioration. The volcanic tuff blocks used in the cornices, pilasters and decorative elements of the church in particular show severe signs of deterioration. After the destruction of the roof of the church in an earthquake in 1812, and exposure of interior of the church to the weather, the volcanic tuff blocks began to deteriorate rapidly. The stones now show severe signs of disaggregation, flaking, cracking, and continuous loss of material. A comprehensive conditions survey of the stones, and documentation of past restoration efforts in December, 1993, determined the most significant elements and deterioration conditions to consider in the conservation program.

The project began with a review of the history, use and characterization of consolidation systems for the conservation of stone objects to select the most appropriate materials for the treatment of these stones. Following the selection of the materials for the consolidation of the stones and repair of cracks in the stones, the research group designed an experimental program to characterize the stones and assess the performance of these materials. The materials evaluated in the experimental program will be examined further through an on-site testing program and their performance evaluated at least one year later. Based on the results of these tests, the research group will develop a conservation program for the treatment of the volcanic tuff blocks and their maintenance in the future.



## 4.2 HISTORY OF THE SITE

The Old Stone Church at Mission San Juan Capistrano, completed in 1806, and consecrated as the largest of the California Mission churches, has withstood the action of weather, earthquakes, and several reconstruction campaigns over nearly two hundred years. The church was built under the direction of Isidro Aguilar, a master mason from Culiacan, Mexico. The plan of the church is in the shape of a Latin Cross. The walls of the church incorporate many motifs in the decorative elements of the church, reminiscent of Aztec motifs frequently used in churches in Mexico in the 19th-century. The accounts of the construction of the church identify three locations for the sources of the stones used at the Old Stone Church: a quarry 4-6 miles northeast of the Mission, a quarry 20 miles north of San Capistrano, and a "rocky point near the ocean," now called San Juan Point. The construction of the church, carried out by the indigenous population lasted seven years.

The Old Stone Church was the place of worship for the mission, and local community for only six years. In 1812, an earthquake partially destroyed the tower and roof of the church, killing many worshippers inside. After that date the Serra Chapel, built in 1776, resumed its function as the church of the mission. In the mid-nineteenth century, local enthusiasts attempted to rebuild the walls of the church. Misguided efforts to clear the debris accumulated in the church with explosives, however, resulted in the destruction of three domes over the transept.



By the 1870s, the nave and transept of the church remained completely exposed to the weather.(Fig. 12)

Restoration efforts resumed in 1896 when the Landmarks Club attempted to stabilize and repair the ruins of the Old Stone Church. Rev. St. John O'Sullivan, the pastor of the mission, continued the restoration work from 1910, until his death in 1933. The pastor installed bracing and tie rods in the walls of the apse to prevent further collapse, repointed the walls in the apse and transept, attempted to repair deteriorated stones in pilasters in the transept with compatible mortars, and constructed concrete bases as supports for the pilasters. Restoration work continued after Rev. St. John O'Sullivan's death under the direction of the later pastors of the mission. Cementitious mortar repairs, incompatible with the existing mortars, and adjacent masonry materials, installed since the 1930s have caused considerable damage to the masonry materials at the church. The adobe walls adjoining the east and west walls of the nave were intermittently repaired during this period.(Fig.13)

The most recent conservation studies on the Old Stone Church at Mission San Juan Capistrano began in 1989 with a survey of the church conducted by Kalliope Theoharidou, a conservation architect. Theoharidou carried out an extensive graphic and written survey of the interior of the church, and proposed specifications for the repair of the sandstone and plaster. The specifications in her report focus on the emergency stabilization of the plasters through preconsolidation, consolidation, and mechanical repair of the stones. In 1990,





Roseland Engineering Company and Thirtieth Street Architects designed scaffolding, temporary shoring and temporary roofing for seismic stabilization work, and to accommodate future conservation work. The conservation program proposed in the present study takes Theoharidou's work several steps further, providing a more detailed conditions survey of the stones, an experimental program for testing conservation materials, and recommendations for the conservation of the masonry at the Old Stone Church.



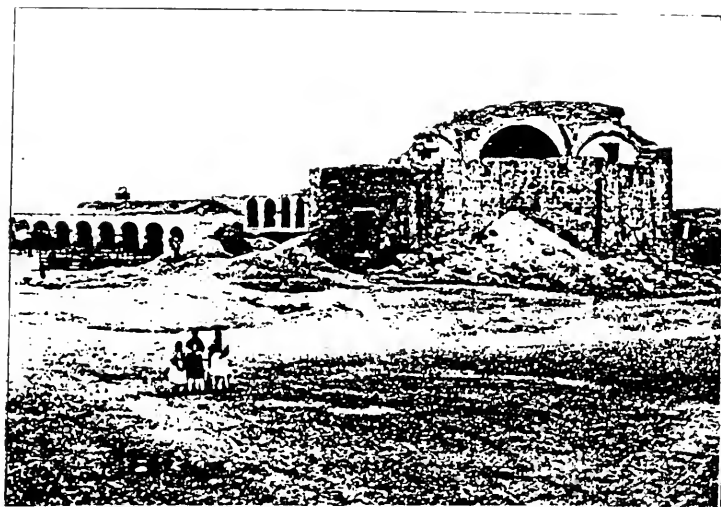


Fig. 12. View of Old Stone Church, Mission San Juan Capistrano, looking northwest (1876).



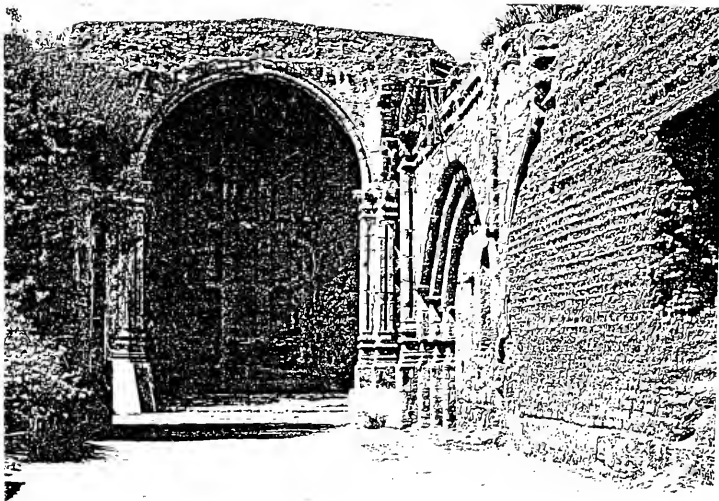


Fig. 13. View of nave of Old Stone Church, Mission San Juan Capistrano (1980).



### 4.3 METHODOLOGY

Phase 1 of the masonry conservation program was initiated with a review of the existing written, graphic, and photographic records related to the history of the Old Stone Church and its restoration efforts. After the initial review of these materials, an extensive architectural investigation of the building was undertaken to record the original construction technology, the nature and extent of subsequent alterations and deterioration, and the current condition of the existing masonry. All current conditions of the interior stonework were recorded as annotations on Theoharidou's recently completed report on the "Conservation and Restoration of Architectural Elements in Sandstone"(1989) at the Old Stone Church. After review and revision of the existing masonry survey, representative samples of tuff, sandstone, plasters and mortars were selected for further examination. Based on the data obtained from the above sources, a laboratory assessment program of possible treatments for the major deterioration mechanisms observed at the site was designed and executed. The results of this test program, together with further on-site testing of the same treatments will provide the data necessary for reassessing the treatments tested. The selected treatment will then be incorporated into a comprehensive conservation program for the site. Additional architectural, engineering, and seismic studies will provide the basis for an overall conservation program for the stabilization of the ruins of the Old Stone Church.





#### 4.4 SITE INVESTIGATION, SAMPLING, AND CONDITIONS SURVEY

A site investigation was carried out by the research team from December 13-20, 1993 in order to complete three tasks: to examine and document the masonry construction techniques and building materials of the church; to study and survey the existing conditions of the stonework and plaster; to initiate the sampling of representative masonry materials (stone, plaster, mortars, and decorative finishes) for their analysis, characterization, and testing of possible treatments in the laboratory. (Figs.14-15) Sampling, and documentation of the masonry materials during site investigation provided the essential information for a comprehensive survey of the conditions of the masonry materials, and the experimental program for testing possible materials for their conservation.

A conditions survey was undertaken to classify and quantify the type and extent of masonry materials and their conditions. The major deterioration mechanisms observed in the stone were identified through petrographic analysis of hand samples, and thin sections of each stone type. Emergency treatments were then carried out to stabilize the plasters and stones in most immediate need of conservation. Following the emergency stabilization program, the survey of the existing conditions of the masonry materials on the interior of the church informed the selection of possible treatments, and their preliminary assessment through an experimental testing program.



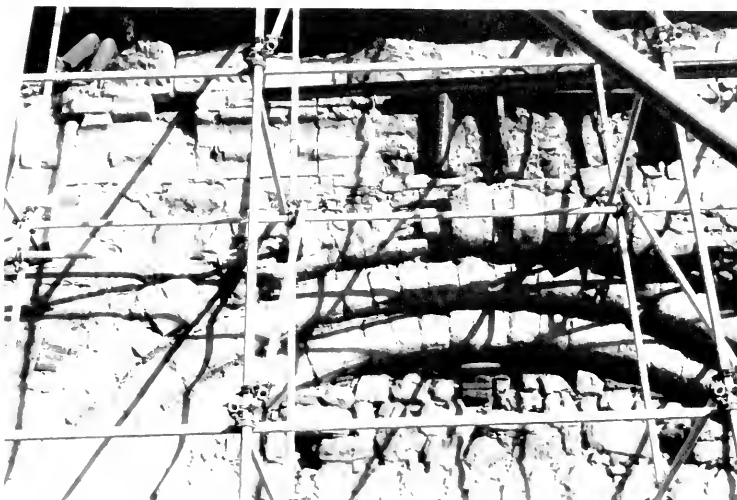


Fig. 14. East wall of nave. Disaggregated and cracking tuff blocks in cornice.



Fig. 15. North wall of east transept. Cementitious mortar repairs on stones, around edges of plaster, and as encasement of pilaster base at north wall of east transept.



## 4.5 EXPERIMENTAL TESTING PROGRAM

A laboratory testing program to evaluate a range of treatment options for the tuff was designed and executed at the ACL from January to July 1994. An aliphatic epoxy resin (EPONEX 1510, Shell Chemical), and an ethyl silicate (CONSERVAR OH, ProSoCo) were applied as consolidants, and an epoxy resin adhesive (EPON 828, Shell Chemical) applied as an adhesive to the test specimens. Standard physico-chemical tests on treated and untreated samples of volcanic tuff and plaster were performed at the ACL and the Laboratory for Research on the Structure of Matter (LRSM). These tests included:

- Water absorption (ASTM-97)
- Bulk specific gravity (ASTM-97)
- Modulus of rupture (ASTM C-99)
- Compressive strength (ASTM C-170)
- Water vapor transmission (ASTM E-96)
- Sodium sulfate crystallization (BRE)
- Shear strength (ASTM D-905)
- Depth of penetration (GCI)
- Accelerated weathering (ASTM D-53)

The results of the tests showed that if applied correctly both EPONEX 1510 and



CONSERVAR OH increase grain-to-grain cohesion and mechanical strength, and cause minimal change in the porosity, permeability and appearance of the stones. EPON 828 injected into stone consolidated with either EPONEX 1510 or CONSERVAR OH proved effective in integrating fragmented masonry.

#### 4.6 MASONRY MATERIALS CHARACTERIZATION

The stonework of the Old Stone Church functions as the primary structural material and also articulates the architectural elements and decorative features on the interior and exterior walls.(Fig. 16) The blocks, either placed in their natural or edge-bedded orientation, parallel or perpendicular to the surface of the wall, are masonry-bonded into the rubble or brick and mortar mix of the wall. The core of the wall is composed of rubble stone in some areas and brick in others, all laid in a lime-based mortar.(Fig. 17) Bricks were used as structural material on the interior face of the wall, in the core at the arches on the east and west walls of the nave, and in the niches in the transept. Terra cotta tiles were similarly used as structural material in the core of the east and west walls of the nave. These tiles, placed flat and at an angle in a lime-based mortar, key into the stones on the exterior face of the wall and into the stone and/or brick on the interior face of the wall. The interior walls are made primarily of dressed sandstone, tuff,





and brick with a lime-based mortar. As on the exterior walls, the ashlar bricks are laid either parallel or perpendicular to the surface of the wall and key into the stone and/or brick and mortar in the core of the wall. The structure of the walls of the transept and the apse is probably similar to the structure of the east and west walls of the nave. The tuff blocks used in the pilasters on either side of the nave and in the cornices, however, do not key into the rubble masonry in the core of the wall. They rest instead on the wall with their bedding alternating from vertical to horizontal. The loss of masonry from the upper levels of coursing in particular has caused not only the exposure of the underlying masonry core to the weather, but also the overall deterioration of the wall structure.



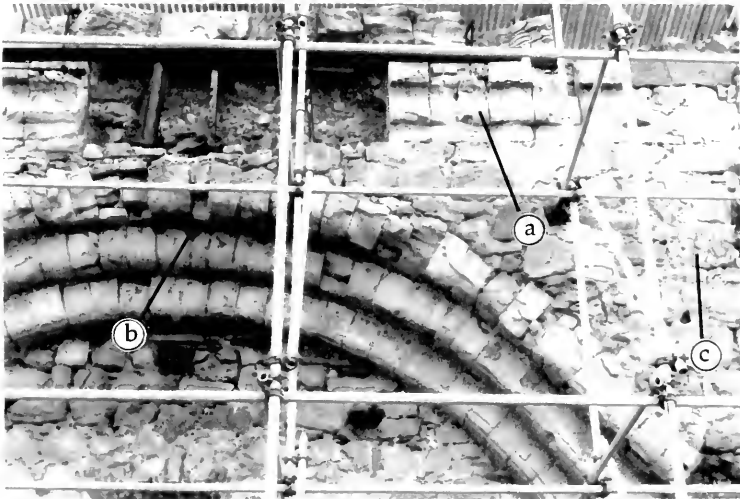


Fig. 16. East wall of nave. Stones in the cornice are volcanic tuff (a) and the stones in the arch are tuff and yellow sandstone (b); the load-bearing stones are yellow and green sandstone (c).





Fig. 17. Cross-section of west wall of nave. The outer and inner face of the wall consists of brick (a), yellow (b) and green sandstone(c), and the core of the wall of rubble stone (d), brick (e) and lime based mortar (f).



#### 4.7 PRETREATMENT CONDITIONS

The present condition of the stonework at the Old Stone Church varies widely from block to block. The variability in the conditions of the stones, attributed to the exposure to weather, inhomogeneity in the geo-physical properties of the stones, and their orientation and location in the building, influences the rate of weathering and mechanisms of deterioration. The present conditions survey of the Old Stone Church has focused on the interior stonework. The exterior stones, primarily green and yellow sandstone, are highly compacted and have resisted weathering well. The walls, architectural details and decorative elements on the interior church are of three types of stones, a volcanic tuff, and green and yellow sandstone. These exhibit considerable differences in their conditions. The volcanic tuff, used primarily in the cornices, pilasters and decorative features exhibits severe conditions (i.e., disaggregation, cracking, erosion, loss, etc.). The previous survey of the interior stones by Kalliope Theoharidou provides an accurate record of the conditions of the interior stonework at the Old Stone Church. These drawings provide the basis for the present conditions survey.

The yellow and green sandstone on the interior of the Old Stone Church show very similar conditions. The stones' location in the building and their bedding orientation in the wall, parallel or perpendicular to the surface, affect the severity of deterioration mechanisms observed. The structure and physical





characteristics of the stones determine their susceptibility to deterioration, whereas the orientation and location of the stones determine the relative action of deterioration mechanisms. The prevailing winds and rain, mainly from north to south and east to west, drive against the stones on the south and east walls of the church. As a result, the stones on these walls of the transept and the west wall of the nave exhibit the most severe conditions. Ground moisture at the foundations of the walls and rising damp appear to have accelerated the deterioration of sandstone blocks at the base of the walls. Sandstone blocks 1-2 ft (30-60 cm.) above grade show signs of disaggregation, flaking and efflorescence due to migration of moisture and soluble salts through the porous stones and continuous wet-dry cycling. The green sandstone, a loosely compacted, heterogeneous sandstone, shows severe disaggregation, flaking, surface erosion and efflorescence above grade. The following terms, based in part on conditions terminology standards developed by the ACL, are recommended for the documentation and description of deterioration mechanisms observed on the site:



<b>Cracking:</b>	Fractures of variable length, width, depth and orientation.
<b>Displacement/ Deformation:</b>	Planar or linear discontinuities defined by (1) uninterrupted deformation or distinct fragmentation in association with cracking or loss within a single element by (2) misalignment of adjoining elements.
<b>Disaggregation:</b>	Active detachment of grains resulting in a rough texture or granular appearance.
<b>Flaking:</b>	The detachment or loss of small thin flakes of stone not necessarily in association with bedding or stone orientation.
<b>Contour scaling:</b>	A localized surficial condition characterized by uneven loss of layers, often of uniform thickness, occurring in a step-like pattern creating contoured depressions of loss. The condition is associated with bedding and stone orientation.
<b>Exfoliation:</b>	The detachment and often partial loss of one or more surface layers of stone parallel to each other and in association with bedding and stone orientation.
<b>Loss:</b>	Absence of original material as judged by incompleteness of form for decoration.
<b>Efflorescence:</b>	White crystalline surface deposits composed of water-soluble salts often found in association with flaking, scaling, exfoliation and loss, and in areas of water penetration.
<b>Biological growth/ Vegetation:</b>	Presence of microflora or higher plant material often found in association with cracks and open joints in areas of high moisture.
<b>Repairs:</b>	Subsequent alterations made for structural, aesthetic, or functional reasons and including mortar and stone repairs.
<b>Open/ Defective Joints:</b>	Complete or partial loss, cracking or separation of mortar within brick or stone joints.



The volcanic tuff blocks, used primarily in the pilasters, cornices and decorative features of the church with beds laid either parallel, perpendicular or diagonal to the surface of the wall, exhibit a variety of conditions. This stone displays considerable variability in its compaction, ranging from a preferred direction of compaction in parallel layers to irregular patterns. The condition of the volcanic tuff blocks therefore varies from block to block as a function of the microstructure of the stone, its physical properties, and orientation and location in the building. The present conditions of these stones include disaggregation, microcracking, severe cracking, flaking, contour scaling, and displacement. The widths of the cracks in the stones range from > 1 mm. to 10 cm. and the depth of the cracks from > 1 mm. to 20 cm.

Many of the mortar repairs, for repointing, for losses in the stones, or for the reconstruction of lost stone elements have caused further damage to the stones, exacerbating existing conditions. In 1910, large areas, mainly in the apse and transept, were repointed in a careless way. Theoharidou states in her report that some of the early patching of decayed stones with cementitious mortar at the west and east pilaster probably belong to this period. The restoration work carried out in this period included the restoration of the moldings at the friezes, cornices, and shaft-bases of these pilasters, as well as the pyramidal reinforcement around their bases. All these interventions were recorded in drawings by the Works Progress Administration in 1936.

Later minor repairs can be recognized by the different materials used for



patching (e.g., cement-lime, or dark, and pure cement mortars) by their color and hardness. Theoharidou observed that the early mortar patches, prior to 1936, have generally adhered well to the stone, and resisted weathering. The adherence of the mortars appears good in the larger patches, while the thin patches have detached from the original stone. The restoration of mission or decayed moldings has been carried out with skill and remains in good condition. Some patches tend to be cracked and detached from the stone, and water has penetrated into existing cracks in the stone. All patches with cement mortar appear problematic. These patches accelerate water penetration, salt crystallization, internal stresses, cracking and disaggregation of the stones and around the repairs.

The conditions of the stones at the Old Stone Church defined above are described and illustrated in the following glossary:

fluorescence





## Cracking

This condition describes three types of cracking in the stones:

(1) **medium to wide cracks** (2 cm. to 10 cm.) are long, continuous cracks which penetrate the stone to a depth of 2-20 cm. These cracks occur in the volcanic tuff blocks and predominate in the upper cornices, pilaster shafts and bases, and around doorways and windows. They appear to be caused by gross structural movement, water penetration, and internal stresses.

(2) **narrow to medium cracks** (1 mm. to 2 cm. in width) penetrate the stones to a depth of 1 mm. to 15 cm.. These cracks predominate in volcanic tuff blocks in the lower and upper tiers of the cornices, pilasters, and around doorways and windows. They also occur extensively in sandstone blocks in the arches on the east and west walls of the nave. These cracks occur in irregular patterns (i.e., map cracking) or align with the preferred direction of compaction or bedding planes and are normally caused by moisture penetration, surface hardening, stresses within the structure of the stone, and structural movement.

(3) **microcracking** (> 1 mm.) is usually localized and confined to a single block. This condition predominates in volcanic tuff blocks and yellow sandstones in irregular patterns (i.e., map cracking) and is normally caused by inherent weaknesses in the stone, moisture penetration, surface hardening, and internal geo-physical stresses.



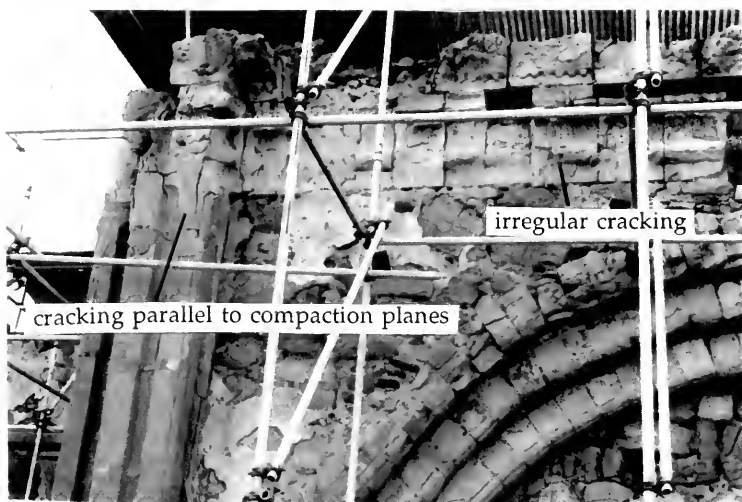


Fig. 18. Cracking of volcanic tuff blocks in pilaster and cornice in east wall of nave.





Fig. 19. Irregular and diagonal cracking of volcanic tuff blocks at intersection of west wall of nave and transept (Photo: Anne Brackin).





Fig. 20. Vertical cracking along bedding planes of tuff at intersection of east wall of nave and transept. Cementitious mortar repair in areas of loss (Photo: Anne Brackin).





## Biological growth/ vegetation

The presence of algae, lichens, and other microflora and higher plant growth may be found either in cracks, open joints, or on the surface of stones in areas of high moisture. Vegetation and plant roots predominate in open joints in volcanic tuff blocks in the upper tier of the cornice in sheltered areas on the west and south walls. A black growth, probably a combination of algae and lichen, predominates in the volcanic tuff in isolated areas exposed to adequate light and moisture at the intersection of walls and on blocks in the lower tiers of cornices.



Fig. 21. Biological growth on tuff at intersection of west wall of nave and transept adjacent to open joints and cracks (Photo: Anne Brackin).



## Flaking

Active detachment and loss of small, thin flakes of stone not necessarily in association with bedding planes or stone orientation. This condition occurs in the green and yellow sandstone and volcanic tuff blocks with their preferred direction of compaction or bedding planes parallel, perpendicular, or diagonal to the surface of the wall. This condition is most severe in the first two courses of stones above the base of walls, in areas exposed to moisture and sunlight, and appears to be related to soluble salt formation.

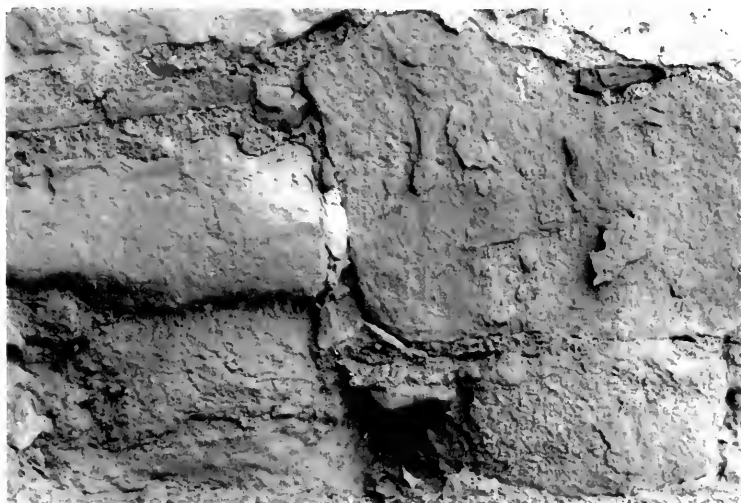


Fig. 22. Flaking of green sandstones above base of wall at north wall of east transept.



## Contour scaling

Localized uneven loss of layers of stone, often of uniform thickness, which occurs in a step-like pattern creating contoured depressions associated with bedding and stone orientation. This condition occurs in volcanic tuff blocks and yellow sandstones with distinct bedding planes parallel, perpendicular, or diagonal to the surface of the wall, in the pilaster capitals and shafts, upper and lower tiers of the cornices, and the arches on the west and east walls of the nave. The condition is most severe in unprotected blocks exposed to light and moisture.



Fig. 23. Contour scaling and flaking of green sandstone 3' above grade at east wall of east transept (Photo: Anne Brackin).



## Exfoliation

This constitutes detachment and loss of one or more surface layers of stone of uniform thickness and parallel to each other in association with bedding and stone orientation. The condition predominates in green and yellow sandstones with bedding parallel to the surface of the wall at the bases of walls and pilasters. It is normally caused by the penetration and capillary rise of ground water, and the formation of soluble salts, and wet-dry cycling.



Fig. 24. Exfoliation of yellow sandstone at base of arch in east wall of nave (Photo: Anne Brackin)





## Loss

Defined as partial or complete loss of stone often in association with exfoliation, disaggregation and previous repairs. This condition predominates in volcanic tuff and sandstone blocks with narrow to wide cracking ( 1 mm. to 10 cm.) or contour scaling. In addition, losses occur in unprotected areas exposed to the weather where disaggregation of the stones leads to surface erosion. All loss results in an incompleteness of form or carved decoration.



Fig. 25. Cracking and partial loss of tuff at cornice level in west wall of nave (Photo: Anne Brackin).



## Displacement/ Deformation

Planar or linear discontinuities are defined by (1) uninterrupted deformation or distinct fragmentation in association with cracking or loss within a single block, or by (2) misalignment of adjoining elements. This condition predominates in volcanic tuff blocks in the cornices, pilasters, and around the doorways in the apse and is normally caused by continuous cracking and gross structural movement.



Fig. 26. Cracking and displacement of tuff at cornice level at east wall of apse (Photo: Anne Brackin).



## Disaggregation

Active detachment of grains resulting in a rough, granular appearance, and overall friability of the stone surface. The condition predominates in unprotected volcanic tuff blocks at the cornices and pilaster capitals and in sandstone blocks at the bases of walls. The causes are usually moisture and salt penetration, and wet-dry cycling.

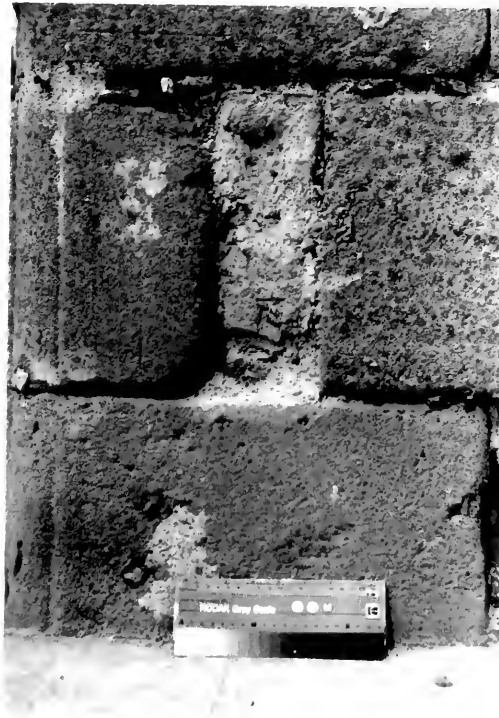


Fig. 27. Disaggregation of tuff at pilaster base at the intersection of the apse and east arm of the transept (Photo: Anne Brackin).



### Open/ Defective joints

Complete or partial loss, cracking, or separation of mortar within the masonry joints. This condition predominates in high exposure and moisture areas in the tuff at the cornices, pilaster capitals and bases, and the sandstone blocks at pilaster bases and arches on west and east walls of the nave. Open or defective joints are normally caused by: moisture penetration and differential expansion and contraction or movement of the mortar within the joints and adjoining stones, efflorescence, and biological growth.



Fig. 28. Open and defective joints at base of pilaster at the intersection of the east transept and east wall of nave (Photo: Anne Brackin).





## Efflorescence

White crystalline surface deposits composed of water-soluble salts, often found in areas of water penetration. This condition predominates in yellow and green sandstone blocks located at the bases of walls and pilasters 1'-2' above grade. The cause is normally the penetration and capillary rise of ground water and associated soluble salts through the stone. As the stone dries, these salts crystallize on or below the surface as cryptofluorescence and present a significant cause of deterioration in sandstone blocks above grade level. The rapid wetting and drying in these areas results in severe exfoliation, contour scaling, and flaking due to the internal disruptive pressures of the crystallized salts in the stone pores.



Fig. 29. Efflorescence on sandstone 1.5' (46 cm.) above grade at northeast wall of apse.



## Previous repairs

Subsequent alterations made for structural, aesthetic or functional reasons, such as mortar patching and stone dutchmen, cracking, flaking, contour scaling and exfoliation. Repairs on the interior of the Old Stone Church occur primarily in volcanic tuff blocks at the cornices, pilaster capitals, shafts and bases, and the doorways and sandstone arches in the apse. Repointing of these mortar joints occurs throughout the interior of the church. The specific locations of the repointing campaigns, however, have not been recorded in previous documentation conditions. The stone behind and around mortar repairs show signs of efflorescence and disaggregation. Some significant losses of stone occur, especially adjacent to cementitious repairs, suggesting a relationship between the inappropriateness of the repair and the condition.

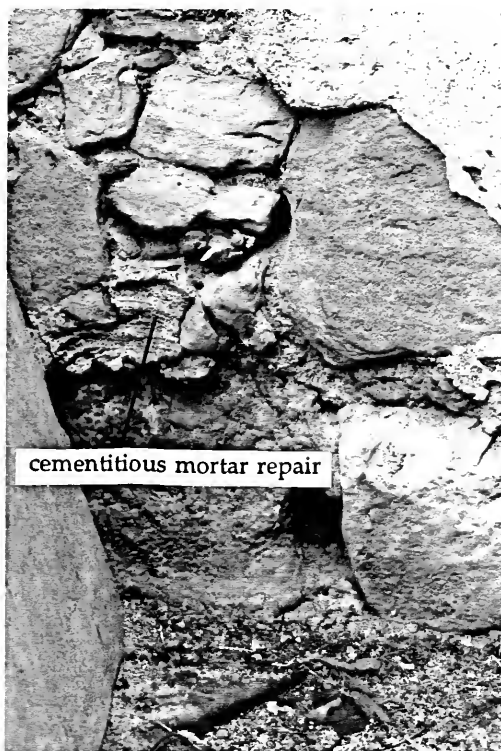


Fig. 30. Cementitious mortar repairs and associated efflorescence above grade at the intersection of the apse and east arm of the transept.



#### 4.8 DIAGNOSIS OF DETERIORATION MECHANISMS

The conditions of the stones at the Old Stone Church vary as a function of their mineralogical composition and physical characteristics as well as their orientation and location in the building. The majority of the masonry materials on the exterior walls, built primarily of green and yellow sandstone have mostly resisted deterioration. The stones on the interior of the church, exposed to the weather for the past one hundred and fifty years, have not performed as well. The tuff blocks in particular have deteriorated badly. Each elevation, exposed to a different set of microclimates, reveals different deterioration conditions and possibly varying rates of weathering. The precise identification and definition of the weathering phenomena affecting each interior elevation will require a long-term study of temperature changes, exposure to rain and sunlight, biological agents and relative humidity and condensation. The current survey of the existing conditions of the stones, nevertheless, provides considerable information on the type, extent, and severity of weathering and decay mechanisms observed on the interior stonework.

The most prevalent and serious condition present in the stones on the interior of the Old Stone Church is cracking. Cracking occurs in both tuff and sandstone blocks in the cornices, pilasters and arches on either side of the nave and transept. The most severe cracks, however, occur in the dressed tuff blocks on the upper and lower tiers of the cornices in the east and west arms of the



transept and nave. The inherent weaknesses in the microstructure of these stones (i.e., loose compaction of euhedral minerals in an ash matrix) allows water to penetrate into the stone easily. The irregularities in the compaction of the minerals in the ash matrix results in irregular cracking of the individual stones. In many areas, the cracking has intersected and penetrated the substrata of the stone and has led to displacement and loss of fragments. In turn, the underlying layers of stones have disaggregated and eroded.

Inappropriate mortar repairs made of cementitious mortar, much harder and denser than the tuff and sandstone, have caused deterioration and also present a significant threat to these stones. These repairs do not allow the underlying mortars or adjacent stones to expand and contract. The differential in the mechanical strength and permeability between the cement repairs, old mortars, and stones result in the penetration and retention of water and soluble salts from the repairs into the masonry materials. Uneven expansion and contraction of these materials during wetting-drying cycles has led to the penetration of moisture behind the cementitious repairs and has increased water absorption. Eventually the formation of deep cracks in the mortar and stones has resulted. The cementitious mortar repairs appear to have caused physical damage and altered the appearance and integrity of the stones.





## **4.9 RECOMMENDATIONS FOR STONE CONSERVATION**

### **COMPREHENSIVE CONSERVATION PROGRAM**

Each condition described in the conditions survey must be addressed in a comprehensive conditions program for the stone. The purpose of the program is to structurally stabilize the stone work, and to restore the legibility of the stones as architectural elements. Deterring further deterioration and retaining the original function of these stones, both as structural and decorative elements, will preserve the architectural integrity of the ruin. The following treatments are recommended for the conservation of tuff stone at the Old Stone Church, based on the existing conditions survey of the stones and the laboratory testing program carried out at the Architectural Conservation Laboratory at the University of Pennsylvania.

### **TEMPORARY EMERGENCY STABILIZATION**

The interior stone of the Old Stone Church exhibits a wide range of conditions that require stabilization in a comprehensive conservation program. Microcracking in particular, has precipitated the penetration of water into the stones and has accelerated their deterioration. These cracks must be filled immediately to deter further deterioration, deep cracking, and the loss of stone



fragments. Many stones will continue to crack and fall if immediate measures are not taken. Emergency measures, which allow for the temporary protection and preservation of the stone, must occur while permanent solutions are field-tested on site for the repair of the cracks and consolidation of the stone. The stones exhibiting microcracking and disaggregation must be stabilized using protective facings and reversible adhesives similar to the facings already applied last year.

### **TEMPORARY STABILIZATION OF BADLY CRACKED AND DISAGGREGATED TUFF BLOCKS**

All friable and badly cracked stones must be temporarily stabilized using protective cotton gauze facings and a dilute solution of reversible adhesive (PVOH, polyvinyl alcohol, followed by a 10% w/v solution of Acryloid B72) to reattach the friable and loose fragments of stone and to keep the stone blocks intact over the next year until full treatment can be effected. In those areas where stones are removed, facings must be applied as well for adequate reinstallation. After reattachment, these facings and adhesives can be entirely removed using appropriate solvents.

These stones must then be permanently stabilized using the recommended consolidant and adhesive and by filling the cracks with a hydraulic lime and aggregate mortar matched in color and texture to the surrounding stone. Friable stones beneath the plasters must be stabilized with the recommended consolidant



and the overlying plaster stabilized and repaired.

## **REMOVAL OF INCOMPATIBLE REPAIRS**

After the preliminary stabilization of the friable and badly cracked stones, incompatible repairs must be removed mechanically. The use of hand tools is recommended to allow precision and control during the removal process and to reduce vibrations which can occur in the mechanical removal of repairs. All cementitious repairs must be removed to prevent further damage unless their removal will cause excessive damage to the underlying stone. Previous repairs will be replaced with hydraulic lime, aggregate mortars, and/or in kind with stone dutchmen depending on the location and damage.

## **REMOVAL OF BIOLOGICAL GROWTH**

The impact of biological growth on the stone is minimal; removal is recommended only in areas where the removal methods will cause insignificant damage to the appearance and physical structure of the stones. A biocide is not recommended at this time. Biological growth must be identified first, and then removed with water, scalpels, and stiff bristle brushes. Vines and higher plants must be removed mechanically to prevent further deterioration of underlying stones.



## **REMOVAL OF SOILING AND SALTS**

The salts and soiling must be removed by non-destructive mechanical methods (e.g., dry brushes, and water and clay or paper pulp poultices). The penetration of salts into the stones will be minimized by the removal of incompatible mortar repairs and filling the cracks with compatible mortars.

## **CONSOLIDATION OF CRACKING AND DISAGGREGATED STONES AND FILLING OF CRACKS**

A representative on-site test area on the south wall of the west transept of the Old Stone Church is suggested for the application of the two systems for the consolidation and adhesive repair of cracks based on the experimental laboratory testing program. The performance of these treatments should be assessed at least one year later.

The experimental program showed that consolidation with EPONEX 1510/ Jeffamine D-230 epoxy resin and injection of EPON 828/ Jeffamine D-230 epoxy resin into cracks provides high mechanical strength, resistance to deterioration, and causes minimal alteration to the stone. The application method, however, is cumbersome and labor intensive. Consolidation with CONSERVAR OH ethyl silicate and adhesive repair with the same epoxy resin, EPON 828/ Jeffamine D-230, imparts properties very similar to the epoxy resin adhesive system. The ethyl silicate consolidant increases the stone's mechanical strength, its resistance





to deterioration, and causes minimal alteration of the stone. The ethyl silicate causes slight discoloration in the stone, but the discoloration disappears with time. Ethyl silicate is also easy to apply. Both the epoxy resin and ethyl silicate, and the adhesive resin are irreversible, however, and must be applied with care.

The epoxy resin consolidant, EPONEX 1510/ Jeffamine D-230, must be applied using bulk procedures (i.e., by a wicking material placed against the face of the stone) or through numerous contact areas to insure adequate depth of penetration and to prevent reverse migration of the resin. In bulk procedures, a wicking material is placed against the face of the stone, the stone is covered with a polyethylene film, and the consolidant is fed into the wicking material from one container and drained off the stone. If the resin is applied through several contact areas, the vesicles containing the epoxy solution must be placed against the face of the stone in a grid pattern. After saturation, the surface of the stone is wiped off with acetone to prevent discoloration. The stone is covered with polyethylene film again and allowed to cure for two weeks.

The alkoxysilane consolidant, CONSERVAR OH, must be applied by brush in three successive cycles, with a 15 minute interval between each cycle. Any excess consolidant remaining on the surface of the stone must be wiped with methyl ethyl ketone. The consolidated stone must then be protected from rain and allowed to cure for two weeks.

After consolidation, the epoxy resin adhesive, EPON 828/ Jeffamine D-230, must then be injected into the cracks, the stone wiped clean with acetone



immediately after injection, and the adhesive allowed to cure for one week. After cure, the upper ½"- 1" of the cracks must be filled with a matched mortar as described above.

The primary cause of deterioration of the volcanic tuff is water penetration, and internal stresses caused by continuous wet-dry cycles and salts. The disaggregated and cracking stone may require additional protection against water penetration. In two selected areas, stones consolidated with epoxy resin and ethyl silicate must be treated with a water repellent to impart water repellency and to reduce the penetration of water into the stones. The methyltrimethoxysilane, Z-6070 (Dow Corning) diluted 1:1 in mineral spirits is recommended as a water repellent. This silane, previously applied on sandstones with high porosity, has been found to be highly effective in decreasing water penetration with visible no alteration of the surface color or shear.

The laboratory results performed thus far show that the ethyl silicate and epoxy resin provide the tuff with similar properties: both consolidants improve the mechanical strength of the stone, and cause minimal change in its permeability and appearance. Although both systems appear to impart the stone with properties that can delay their deterioration, and the epoxy adhesive can fill the cracks and increase the mechanical strength of the stones, it is necessary to apply further laboratory tests for more conclusive evidence on the performance of both systems. These tests may be carried out in conjunction with the application of these materials to a test area at the site of the Old Stone Church.



## INFILLING LARGE CRACKS AND AREAS OF LOSS

In the test area, cracks in the stone too wide for adhesive repair with the epoxy resin must be filled with mortar as described above. In some areas, stone dutchmen with replacement tuff may be necessary for visual or structural integration.

## MAINTENANCE

The conserved stones will require a long-term maintenance program for the evaluation of the treatments and reoccurring deterioration. The consolidants and adhesives recommended in this program are irreversible; the long-term effects of the treatments on the properties and rate of deterioration of the stone must therefore be monitored over at least one year. After the evaluation of the treatments on the test areas, recommendations will be made for the full-scale conservation of the stones. A maintenance program should be included in the final report, written after the consolidation treatment of the tuff blocks. The maintenance program may consist of yearly visual inspections of the stones and documentation of their conditions (e.g., monitoring water repellency). The reoccurrence of any conditions described in the conditions survey could then be



treated with the recommended consolidant, adhesive water repellent and mortar repairs. The most significant properties to monitor include the visual appearance and cracking of the stones. These monitoring program will require both laboratory and field techniques. For laboratory analysis of the stones, cores taken from the representative stones must be analyzed for color change, and water vapor permeability. A chromameter must be used to measure and monitor the appearance of the stones. The permeability of the stones may be measured measuring the change in the water absorption of the stones. The conditions of the stones may be analyzed through regular visual inspections of their appearance.





## APPENDIX A

### LIST OF RECENT STUDIES ON THE USE OF EPOXY RESINS AND SILICONE ESTERS FOR STONE CONSERVATION

#### EPOXY CONSOLIDANTS AND ADHESIVES

Alessandrini, G., R. Peruzzi, "Control of the Behavior of Two Epoxy Resins for Stone Treatments," in *Deterioration and Protection of Stone Monuments, Proceedings of the RILEM International Symposium, Paris, June 5-9, 1978*, 6.1. Paris: Centre Experimental de Recherches et d'Études du Bâtiment et des Travaux Publiques, 1978.

*stones tested:* marble (Candoglia, Italy), sandstone (Arezzo, Italy), tuff (Bolsano, Italy).

*products tested:* epoxy resin, Araldite XG 40, with hardener XG 41; epoxy resin, Araldite PZ 820, with the hardener HZ 820.

*tests performed:* water absorption, density, pore size distribution, SEM examination, accelerated weathering.

Cavalletti, R., L. Lazzarini, L. Marchesini, and G. Marinelli, "A New Type of Epoxy Resin for the Consolidation of Badly Decayed Stones," in *Deterioration and Conservation of Stone, Fifth International Congress, Lausanne, September 25-27, 1985*, 769-778. Lausanne, Switzerland: Presses Polytechniques Romandes, 1985.

*stone tested:* limestone (Vicenza, Verona and Istria, Italy), monzonite marble (Ezine, Turkey), marble (Marmara Is., Turkey), volcanic tuff (Viterbo, Italy)  
*products tested:* 25% sol. cycloaliphatic diglycidyl epoxy resin, EP2102, in a mixture of toluene and isopropanol and aliphatic polyamine hardener, K2102; methacrylate ethylmethacrylate copolymer, Acryloid B72 (Rohm & Haas).

*tests performed:* accelerated weathering, color measurement with Photovolt Reflection Meter (model 610); density, SEM examination, hydrochloric acid test, water absorption, resistance to salt crystallization, compressive strength, *in situ* treatments.



Clifton, James. "Laboratory Evaluation of Stone Consolidants," in *Adhesives and Consolidants, Preprints of the Contributions to the Paris Congress, September 2-8, 1984*, 51-55. London: IIC, 1984.

*stones tested:* sandstone (Briar-Hill), limestone (Indiana)

*products tested:* silicone, sodium methyl silicate, experimental fluoride, epoxy, silane, experimental silicone, polyurethane, aqueous fluoride, butyl acrylate, acrylic ester, methyl acrylate, silane, fluoride salt and methyl methacrylate.

*tests performed:* tensile strength, compressive strength, depth of penetration by surface reflectance, visual examination, resistance to acid precipitation, resistance to freeze-thaw cycles, thermal expansion.

Cuttano, M., P. Mastronardi, and R. Rossi Manaresi. "Alveolar Weathering of the Tuff of Matera; Mechanism of Decay and Effective Preservative Treatment," in *The Conservation of Stone II. Preprints of the Contributions to the International Symposium, Bologna, 27-30 October 1981*, volume 2, 335-377. Bologna: Centro per la Conservazione delle Sculture all'Aperto, 1981.

*stone tested:* biocalcarene tuff

*products tested:* mixture of ethyl silicate and alkyltrialkoxysilane; 15 % sol. methyl phenylpolysiloxane, Rhodorsil XR-893 (Rhône Poulenc) in toluene; silicone product, Rhodorsil AC-30 (Rhône Poulenc), undiluted; 45% sol. PEMA-PMA copolymer, Acryloid B72 (Rohm & Haas), and 3.5% silicone, DRI FILM 104 (General Electric), in chloroethane acetone; silicate acrylic copolymer, Product 460 (Mased), in water; epoxy monomer, Product XG40-G41 (Ciba Geigy); pentaeritic tetraglycidyl ether and cycloaliphatic hardener; aluminum stearate, Transkote (Sandtex), in aromatic solvent; 20% sol. aluminum magnesium fluorosilicate, Banafluorato (Ital-Bavia), in water.

*tests performed:* porosity, bulk density, compressive strength, water absorption, saturation coefficient, capillarity.

De Witte, E., A. E. Charola, and R. P. Sherryll, "Preliminary Tests on Commercial Stone Consolidants," in *Deterioration and Conservation of Stone, Fifth International Congress, 25-27 September 1985, Lausanne*, 709-723. Lausanne, Switzerland: Presses Polytechniques Romandes, 1985.

*stone tested:* limestone

*products tested:* ethyl silicate, Stone Strengthener OH; mixture of ethyl silicate and methyltrimethoxysilane, Stone Strengthener H; ethyl silicate,



Tegovkan V; mixture of ethyl silicate and methytrimethoxisilane, Tegovkan T; methyl propylsiloxane, Gevicol M; silicic acid, ISO 110; potassium silicate, Gay wall; fluorosilicate, Bargat; polyurethane, Desmodur E3150; epoxy resin, PC 5001; epoxy resin, Episol; polymethacrylate, Thoroglaze.  
*tests performed:* micro-water droplet test for measurement of impregnation depth, capillary rise, visual interpretation of color change, SEM examination.

Domaslowski, W., "L'Affermissement Structural des Pierres des Solutions à Base de Resins Thermoplastiques," in *Preprints of the Contributions to the New York Conference on Conservation of Stone and Wooden Objects, 7-13 June 1970*, 85-93. London: IIC, 1971.

*stones tested:* sandstones (Nietulisko and Zerkowice, Poland)  
*products tested:* 5, 10, 20, 30% sol. epoxy resin, Epidian 5, with various solvents, including xylene, isopropanol, benzene, toluene, methanol, xylene, dioxan, ethylglycol, acetone, butanone and cyclohexanone.  
*tests performed:* cure time, capillary rise, compressive strength, water absorption, density, open porosity, accelerated weathering.

Domaslowski, W., "Consolidation of Stone Objects with Epoxy Resin," in *Monumentum*, 4 (1969): 51-64.

*stones tested:* siliceous sandstone, soft limestones  
*products tested:* 16-52% sol. epoxy resin, Epidian 1-5, and 18% sol. hardener, TETA, with different combinations of solvents, including xylene, toluene, benzene, cyclohexane, methyl ethyl ketone, ethyl glycol and alcohol.  
*tests performed:* bulk density, open porosity, water absorption, compressive strength, frost resistance, water resistance.

Domaslowski, W., "La Consolidation des Structures de Grès à l'Aide de Resins Thermoplastiques," in *Deterioration and Preservation of Stone, Proceedings of the Fifth International Congress, Lausanne, September 25-27, 1985*, 727-738. Lausanne, Switzerland: Presses Polytechniques Romandes, 1985

*stones tested:* sandstones (Nietulisko and Zerkowice, Poland)  
*products tested:* polymethyl methacrylate (PMM);PEMA-PMA copolymer Acryloid B72 (Rohm & Haas).  
*tests performed:* evaluation of the separation of phases of solutions containing toluene and solutions mixed with white spirit; evaluation of distribution of resins in the structure of the consolidated stone.



Domaslowski, W., and Alijia Strelezyk, "Evaluation of the Applicability of Epoxy Resins to Conservation of Historic Stone Monuments," in *Case Studies in the Conservation of Stone and Wooden Objects*, Bologna, 21-26 September 1986, 126-132. Bologna: 1986.

*stones tested:* sandstone with argillaceous binder (Nietulisko, Poland)

limestone with silica-argillaceous binder (Pinezow, Poland)

*products tested:* 10% sol. epoxy resin, Epidian 5, and hardener, Z-1, in mixture of toluene and methanol; 15% sol. epoxy resin, Epidian 5, in toluene and methanol

*tests performed:* resistance to microbial growth.

Domaslowski, W., and J. Lehman, "Recherches Sur l'Affirmissement Structural des Pierres au Moyen des Solutions de Resins Thermoplastiques," *The Treatment of Stone: Proceedings of the Joint Committee for the Conservation of Stone*, Bologna, October 1-3, 1971, 255-272. London: IIC, 1986.

*stone tested:* sandstone (Nietulisko and Zerkowice, Poland)

*products tested:* 5, 10, 15, 20% sol. butyl polymethacrylate in white spirit.

*tests performed:* density, water absorption, compressive strength, tensile strength, evaporation temperature, porosity.

Down, J. L., "The Yellowing of Epoxy Resin Adhesives: Report on High Intensity Light Aging," *Studies in Conservation*, 29 (1984): 63-76.

*material tested:* glass plates

*products tested:* 47 epoxy resin adhesives with varying chemical compositions

*tests performed:* measurement of absorption UV light, infrared light spectrophotometry.

Down, J. L. "The Yellowing of Epoxy Resin Adhesives: A Report on Natural Dark Aging," *Studies in Conservation*, 31 (1986): 100-101.

*material tested:* glass slides

*products tested:* 54 commercial products of diglycidyl ether of bisphenol A epoxy resin

*tests performed:* measurement of absorption UV light, infrared light spectrophotometry.





Gauri, K. Lal, and Madiraju V. Appa Rao, "Certain Epoxies, Fluoro-carbon Acrylics and Silicones as Stone Preservatives," *Geological Society of America, Engineering Geology Case Histories* 11 (1978): 73-79.

*stone tested:* limestone

*products tested:* silicone resins (Dow Corning, Mobay Chemical, Union Carbide); fluorocarbon acrylics (Du Pont); epoxies (Celanese coatings).

*tests performed:* resistance to acid precipitation, compressive strength, water absorption.

Gauri, K. Lal, "Conservation of the California Building, San Diego, U.S.A.: A Case History," in *Deterioration and Protection of Stone Monuments, RILEM International Symposium, Paris, 5-9 June, 1978*, 7-5. Paris: Centre Éxpérimental De Recherches et d'Études du Bâtiment et des Travaux Publiques, 1978.

*stone tested:* cast stone

*products tested:* 15% sol. bisphenol A solution in acetone and diethylene triamine; fluoropolymer-B (Du Pont).

*tests performed:* compressive strength, water absorption, water vapor permeability.

Gauri, K. Lal, "Efficiency of Epoxy Resin Adhesives as Stone Preservatives," *Studies in Stone Conservation*, 19 (1978): 100-101.

*stone tested:* marble (Carrara, Italy)

*products tested:* epoxy resin, Epi-Rez 502 (Calenese coatings).

*tests performed:* accelerated weathering with SO<sub>2</sub>.

Gauri, K. Lal, "Reactivity of Treated and Untreated Marble Specimens in an SO<sub>2</sub> Atmosphere," *Studies in Conservation*, 18 (1973): 25-35.

*stone tested:* marble

*products tested:* epoxy resins in various concentrations.

*tests performed:* accelerated weathering with SO<sub>2</sub>, x-ray diffraction and fluorescence examination.



Ginnel, W. S., P. Kotlik, C. Selwitz, and G. S. Wheeler, "Recent Developments in the Use of Epoxy Resins for Stone Consolidation," Report of Getty Conservation Institute, 1994.

*stone tested:* limestone (Salem, Indiana)

*products tested:* 16% sol. epoxy resin, Araldite GY6010 (Ciba Geigy) ,and hardener, HY956 (Ciba Geigy), in toluene and isopropanol; 16% sol. epoxy resin, Eponex 1510 (Shell), and hardener, Jeffamine D-230 (Texaco), in toluene and isopropanol.

*tests performed:* appearance measurement by using Minolta CM1000 chromameter, accelerated weathering, natural weathering.

Jaton, C., A. Boineau, R. Coignard, "Experimental Treatment of Rocks," in *Deterioration and Conservation of Stone Objects, Fourth International Congress, Louisville, KY, 7-9 July 1982*, 205-217. Louisville, KY: University of Louisville, 1982.

*stones tested:* limestone, sandstone and granite

*products tested:* Epoxy resin, Sol 28/15 (Sinmast); Polyacrylamide (Durox), ethyl silicate, Wacker OH (Wacker-Chemie); alkoxysilane, Silane XR 54802 (Rhône Poulenc); PEMA-PMA copolymer, Acryloid B72 (Rohm & Haas).

*tests performed:* porosity, capillarity, density, freeze-thaw resistance, modulus of elasticity, compressive strength, tensile strength, abrasion resistance, water vapor permeability, accelerated weathering.

Kotlik, P., P. Justa, and K. Zelinger. "The Application of Epoxy Resins for the Consolidation of Porous Stone," *Studies in Conservation* 28, 2 (1983): 73-79.

*stone tested:* siliceous sandstone (Horice, Bohemia).

*products tested:* Several epoxy resins based on bisphenol A with various molecular units with hardeners, diethylene triamine (DETA) and Aminoamide D 500.

*tests performed:* capillary rise, density, depth of penetration.

Laukhuf W., C. A. Plank, and K. Lal Gauri. "Mechanisms of SO<sub>2</sub> Absorption in Epoxy Resins," in *Deterioration and Preservation of Stone Objects, Fourth International Congress, Louisville, Kentucky, 1982*, 239-241. Louisville, KY: University of Louisville, 1982.

*stones tested:* marble

*products tested:* epoxy resin, Epi-Rez 502 (Coatings Company); epoxy resin,



Epi-Rez 510 (Coatings Company).

*tests performed:* SO<sub>2</sub> adsorption by infrared spectrophotometry, pore size distribution.

Moncrieff, A., "The Treatment of Deteriorating Stone with Synthetic Resins. A Further Report," in *Deterioration and Preservation of Stones, Proceedings of the Fourth International Congress, Louisville, Kentucky, July 7-9, 1967-1972*. Louisville, KY: University of Louisville, 1982.

*stone tested:* marble and limestone

*products tested:* epoxy resin, AY 103/X537; polyurethane coating, X54-802; triethoxymethylsilanes, Tegovakon ICI, EP 5850 and Wacker VP301.

*tests performed:* natural weathering

Munnikendam, R. A., "A New System for the Consolidation of Fragile Stone." *Studies in Conservation*, 18 (1973): 95-97.

*stones tested:* tuff and sandstone

*products tested:* 10% sol. PEMA-PMA copolymer, Acryloid B72 (Rohm and Haas) and Bedacryl 122-x (ICI) in toluene; ethyl silicate, "Steinverfestiger" (The. Goldschmidt); 10% sol. epoxy resin and hardener, Epon 828/DETA (Shell) in a mixture of toluene and methanol; Bagrat-150-110-clear (Hoesch-Chemie)

*tests performed:* sodium sulfate crystallization, accelerated weathering.

Rossi-Manaresi, R., G. Alessandrini, S. Fuzzi, and R. Peruzzi, "Assessment of the Effectiveness of Some Stone Preservatives for Marbles and Limestones," in *Third International Congress on the Deterioration and Preservation of Stone, Venice, 24-27 October 1979*, 357-376, Padova: Università degli Studi, Istituto di Chimica Industriale, 1979.

*stones tested:* limestone (Istria, Italy), limestone with calcareous nodules (Verona, Italy)

*products tested:* 30% sol. acrylic-polymer-silicone, Product E0073 (ARD-Raccanello), in diluene E0074 (ARD Raccanello); 35% sol. acrylic polymer, "Incolore per marmi 11.21" (Duco Montedisio) in toluene and xylene; 15 parts 30% sol. PEMA-PMA copolymer, Acryloid B72 (Rohm & Haas), in Nitrodiluent; 5 parts 70% sol. silicone, 104 (General Electric) in white spirit and 40 parts chloroethane (1,1,1-trichloroethane).

*tests performed:* porosity, bulk density, compressive strength, water absorption, capillarity, saturation coefficient, accelerated aging tests in the



presence of SO<sub>2</sub>, SEM examination.

Rossi-Manaresi, R., and R. Pelizzer. "The Volcanic Tuff of the Archaeological Monuments of Cochasqui, Equador: Causes of Decay and Effectiveness of Conservation Treatments," in *Deterioration and Preservation of Stones, Third International Congress, Venice, 24-27 October 1979*, 605-611. Padova: Università degli Studi, Istituto di Chimica Industriale, 1979.

*stones tested:* volcanic tuff

*products tested:* ethyl silicate, Silester ZNS (Pietrocarini), in ethanol; aluminum staerate, Transkote (Sandtex), undiluted; mixture of Silester and Transkote.

*tests performed:* bulk density, compressive strength, water absorption, saturation coefficient, capillarity.

Sleater, G., "Development of Performance Criteria for the Selection of Stone Preservatives," *Geological Society of America Engineering Geology Case Histories* 11 (1978): 65-71.

*stones tested:* marble, limestone, sandstone

*products tested:* acrylics, acid fluorides, epoxies, ethyl silicate, fluorocarbons, limewater, methacrylate, silicones, sodium silicate and sodium silicones.

*tests performed:* density, measurement of appearance with colorimeter, water absorption, water-vapor permeability, abrasion resistance, surface hardness

Tennent, N. H., "Clear and Pigmented Epoxy Resins for Stained Glass Conservation: Light Aging Studies," *Studies in Conservation*, 24 (1979): 153-164.

*products tested:* Six bisphenol A epoxy resins, Araldite AY103/HY951, Plastogen EP, Thermoset 600/No.64 + Accelerator, Epotek 301, Araldite MY790/X83-319 + Flexibilizer DY040 and Ablebond 342-1.

*tests performed:* Ageing tests, infrared spectroscopic examination, yellowing Index, visual inspection.

Wheeler, G. S., S. A. Fleming, and S. Ebersole, "Comparative Strengthening Effect of Several Stone Consolidants on Wallace Sandstone," *Deterioration and Conservation of Stones, Seventh International Congress, Lisbon, Portugal, 15-18 June 1992*, 1033-1038. Lisbon, Portugal: Laboratorio Nacional de Engenharia Civil, 1992.





*stones tested:* purely calcitic limestone (Salem, Indiana, U.S.A.), silica cemented sandstone (Wallace, Nova Scotia, Canada)

*products tested:* ethyl silicate, Wacker OH; mixture of ethyl silicate and polysiloxane, Wacker OH; PEMA-PMA copolymer, Acryloid B72, and methyltrimethoxysilane (MTMOS) in toluene; epoxy resin, Epo-tek 301; an isocyanate and several systems based on MTMOS and trimethoxysilane coupling agents.

*tests performed:* tensile strength

## ALKOXYASILANES

Ausset, P., J. Philippon, "Essai d'Évaluation de Profondeur de Pénétration de Consolidants de la Pierre," in *Deterioration and Conservation of Stones, Fifth International Congress, Lausanne, September 25-27, 1985*, 524-533. Lausanne, Switzerland: Presses Polytechniques Romandes, 1985.

*stone tested:* limestones

*products tested:* methyl trimethoxysilane, Z6070 (Dow Corning); ethyl silicate, Wacker OH; mixture of ethyl silicate and polysiloxane, Wacker H; organosilane oligomer, Wacker 290L (Wacker Chemie).

*tested performed:* electronic microscopic examination of depth of penetration *in situ*.

Bianchetti, P.L., and G. Lombardi, "Study of the Degradation of "Tuff" Blocks Used in the Roman Temple of Cibeles," in *Deterioration and Preservation of Stones, Fourth International Congress, Louisville, KY, July 7-9 1982*, 29-38. Louisville, KY: University of Louisville, 1982.

*stone tested:* tuff

*products tested:* ethyl silicate, Wacker OH (Wacker-Chemie); ethyl silicate, mixture of ethyl silicate and polysiloxane, Wacker H (Wacker-Chemie).

*tests performed:* porosity, bulk density, water absorption.

Domaslowski, W., "Possibilities of Silica Application in the Consolidation of Stone Monuments." in *Proceedings of the Third International Congress on the Deterioration and Conservation of Stone, Toruń, September 12-14, 1988*, 563-575. Toruń, Poland: Nicholas Copernicus University, 1988.



*stones tested:* limestone, sandstone

*products tested:* 10, 20, 30% sol. water glass; 30% sol. zinc fluorosilicate; alkoxypolysiloxane, Steinfestiger OH (Wacker Chemie).

*tests performed:* capillarity, removal of sodium ions from water glass by univalent hydrogen ions, compressive strength, tensile strength, water absorption, accelerated weathering

Laurenzi Tabasso, M., and V. Santamaria, "Consolidant and Protective Effects of Different Products on Lecce Limestone," in *Deterioration and Preservation of Stones, Proceedings of the Fifth International Congress, Lausanne, 25-27 September 1985*, 697-707. Lausanne, Switzerland: Presses Polytechniques Romandes, 1985.

*stone tested:* limestone (Lecce, Italy)

*products tested:* ethyl silicate, Wacker OH; PEMA-PMA copolymer, Acryloid B72, in methyl phenol polysiloxane, Rhodorsil 11309 (Rhône Poulenc); perfluoropolyether, Foblin Y Met (Montefluos S.p.A.); oligomeric polysiloxane, Wacker 290L, in nafta, diacetone alcohol and 1,1,1-trichloroethane.

*tests performed:* density, appearance by Munsell Color Charts, compressive strength, water absorption, water vapor permeability, evaporation rate, porosity, pore size distribution, accelerated weathering.

Rossi-Manaresi, R., "Causes of Decay and Conservation Treatments of the Tuff of Castel dell'Ovo in Naples," in *Deterioration of Building Stones, Proceedings of the Second International Symposium, Athens, September 27-October 1, 1976*, 233-248. Athens: Publication Division of the Greek National Group of IAEG, 1976.

*stone tested:* tuff

*products tested:* siliconate-acrylic copolymer, Product 640, in water; mixture of ethyl silicate alkytrialkoxysilane, Wacker H; 15% sol. methylphenylpolysiloxane, Rhodorsil XR-893, in toluene; 15% sol. methylphenylpolysiloxane, Rhodorsil 10336, in toluene, and a mixture containing 1 part PEMA-PMA copolymer, Acryloid B72, in toluene and xylene; 1 part silicone, Dri Film 104, in organic solvent and 8 parts chloroethene (1,1,1-trichloroethane).

*tests performed:* density, porosity, water saturation, water absorption, depth of penetration by water droplets, capillarity, accelerated weathering.



Rossi-Manaresi, R., and A. Tucci, "SEM Examination of a Biocalcarene Treated with Acrylic Polymers, Silane or Silicone Resins," in *Deterioration and Preservation of Stones, Fifth International Congress, Lausanne, 25-27 September 1985*, 871-880. Lausanne, Switzerland: Presses Polytechniques Romandes, 1985.

*stone tested:* fossiliferous limestone

*products tested:* 10% sol.methyl phenyl polysiloxane, Rhodorsil 11309 (Rhone-Poulenc), in toluene; methyl trimethoxysilane (MTMOS), Silane Z-6070 (Dow Corning); 7% sol. prepolymerized methyl alkoxysilane, Dri Film 104 (General Electric), in xylene, toluene, acetone and 1,1,1-trichloroethane; 10% sol. PEMA-PMA copolymer, Acryloid B72 (Rhom & Haas), in mixture of acetone, 1,1,1-trichloroethane, xylene and toluene; methyl methacrylate-butylmethacrylate copolymer, Safe Stone (Sinco Mec Kolor), in white spirit.

*tests performed:* density, capillarity, water absorption, SEM examination.

Valdeon, L., C. Grossi, R. Marcos, and R. Esbert, "Effects of Consolidation Treatments on Hydric Properties of Stones," in *Deterioration and Conservation of Stones, Seventh International Conference, Lisbon, Portugal, 15-18 June 1992*, 1073-1081. Lisbon, Portugal: Laboratorio Nacional de Engenharia Civil, 1992.

*stones tested:* dolomite, limestone, sandstone

*products tested:* polysiloxane (protective); polyurethane (protective); ethyl silicate (consolidant) and oligomeric polysiloxane (protective); ethyl silicate (consolidant) and polyurethane (protective).

*tests performed:* water absorption, capillary rise.

Weber, H. "Conservation and Restoration of Natural Building Stone in Europe," *APT Bulletin*, XVII, 2 (1985): 15-23.

*stones tested:* sandstone

*products tested:* ethyl silicate, Wacker OH; mixture of ethyl silicate and silane, Wacker H.

*tests performed:* water absorption, water vapor permeability and porosity of drill cores from building

Weber, H., "Stone Conservation and Consolidation: Salzburg's Franziskanerkirche," *APT Bulletin*, XX, 3 (1988): 23-29.

*stone tested:* sandstone

*products tested:* ethyl silicate, Wacker H; mixture of ethyl silicate and silane,



Wacker OH; silicone resin water repellent, Wacker 190, in organic solvents; siloxane water repellent, Wacker 290, in organic solvents.  
*tests performed:* water absorption, depth of penetration, capillarity.

Zinsmeister, K., N. Weiss, and F. Gale, "Laboratory Evaluation of Consolidation Treatment of Massillon (Ohio) Sandstone," *APT Bulletin*, XX, 3 (1988): 35-39.

*stone tested:* sandstone (Massillon, Ohio)

*product tested:* ethyl silicate, Conservar H, OH (ProSoCo).

*tests performed:* porosity, density, water absorption, compressive strength, tensile strength, abrasion resistance.





## APPENDIX B

### PROCEDURES FOR TESTS PERFORMED IN EXPERIMENTAL PROGRAM

#### 1.1 MODULUS OF RUPTURE

**Based on Test:** ASTM C99-87  
"Standard Test for Modulus of Rupture  
of Dimension Stone"

**No. Specimens**  
**@ Test:** 3 (2 Consolidants, 1 Control)  
**TOTAL:** 9

#### TIME REQUIRED

**Consolidation:** 21 days  
**Test:** 1 day  
**TOTAL:** 22 days

#### *Significance and use*

This test method is useful in indicating the differences in modulus of rupture of dimension stones. This test also provides one element in comparing stones of the same type.

#### *Apparatus*

Testing machine - the accuracy of the testing machine must be within 1% range from 10 to 1000 lbf (44 to 4450 N).

Knife edges - the supports for the specimens must be two knife edges of the rocker type with edges at least as long as the length of the specimen.

#### *Test specimens*

The standard size for specimens is approximately 10 by 20 by 5.6 cm. (4 by 8 by 2 1/4 in) and three or more must be prepared for each desired condition of loading. They must be sawed from the sample and finished by grinding smooth surfaces. The 10 by 20 cm. faces shall be as nearly plane and parallel as practicable.



### *Procedure*

Lay the specimen flatwise on the supporting knife edges, spaced 17.5 cm. (7 in.) apart and equidistant from the loading knife edges, with all three knife edges parallel. When a load of 10 lbf (44 N) has been applied, stop loading and make all knife edges coincide with the marks on the specimen by centering the specimen under the loading edge and moving the supporting edges under the span marks. Apply the load at a rate not exceeding 1000 lbf/min. (4450 N/min.) until failure of the specimen.

### *Calculation*

Calculate the modulus of rupture of each specimen as follows:

$$R = 3Wl/2bd^2$$

where:

R = modulus of rupture, Mpa (or psi),

W = breaking load, N (or lbf),

l = length of span, mm. (or in.),

b = width of specimen, mm. (or in.).

### *Report*

Report the average of all values of rupture for test specimens loaded perpendicular to the rift as the modulus of rupture perpendicular to the rift, and report the average value of all test specimens loaded parallel to the rift as the modulus of rupture parallel to the rift. If a specimen gives a value as much as 20% under the average it shall be examined for defects and, if the low value appears to be due to a flawed or faulty test piece, report the average of the remaining specimens of the group as the modulus of rupture of the sample for the condition of loading under consideration.

### *Precision and Bias*

Individual variations in a natural product may result in deviation from accepted values. A precision section will be added when sufficient data are available to indicate acceptable tolerances in repeatability and reproducibility.



## 1.2 COMPRESSIVE STRENGTH

**Based on Test:** ASTM C170-97  
"Standard Test Method for Compressive  
Strength of Dimension Stone"

**No. Specimens:**  
**@test:** 4 (2 Consolidants, 1 Control)  
**TOTAL:** 12

### TIME REQUIRED

**Consolidation:** 21 days  
**Test:** 1 day  
**TOTAL:** 22 days

### *Significance and Use*

This test method is useful for indicating differences in compressive strength between various types of dimension stones. This test method also provides one element in comparing stones of the same type.

### *Apparatus*

In vertical testing machines, the spherical bearing block shall be suspended from the upper head of the machine in a manner that the contact plate remains in a central position (spherical surface in full contact) when not loaded. The spherical surfaces shall be well lubricated, and the center of the curvature shall lie in the surface of contact with the specimen

### *Test specimens*

The test specimens may be cubes, square prisms or cylinders and shall be cut from the samples with saws or core drills. The diameter or lateral dimension shall not be less than 5 cm. (2 in.) and the ratio of the height to the diameter or lateral dimension shall not be less than 1: 1. At least five specimens shall be prepared for each condition of the test. The load-bearing surfaces shall be finished by grinding as nearly true and parallel planes as practicable.

The load-bearing surfaces and the direction of bedding (or rift) shall be marked on each specimen after finishing. The load bearing areas shall be



calculated from measurements taken midway between the load-bearing surfaces. The dimensions of the specimens shall be measurements taken midway between the load-bearing surfaces.

#### *Procedure*

Center the specimens in the testing machine and apply the initial load at the rate that will permit hand adjustment of the contact plate on the specimen. Rotate the specimen back and forth through an angle of about 30° under a small load to properly seat the spherical block, but take care not to move the specimen out of the central position. Preferably, the rate of loading should not exceed 690 kPa (100 psi)/s, but this requirement may be seen as met if the speed of the loading head is not more than 1.3 mm. (0.05 in.)/min.

#### *Calculation*

Calculate the compressive strength of each specimen as follows:

$$C = W/A$$

where:

C = compressive strength of the specimen, Mpa (psi),

W = total load, N (lbf), on the specimen at failure, and

A = calculated area of the bearing surface mm.<sup>2</sup> (in.<sup>2</sup>),

Round each result to the nearest 1 Mpa (100 psi).

#### *Report*

The average compressive strength of all specimens loaded shall be reported as the compressive strength parallel or perpendicular to the bedding (or rift).

#### *Precision and Bias*

Individual variations in a natural product may result in deviations from accepted values. A precision section will be added when sufficient data are available to indicate acceptable tolerances in repeatability and reproducibility.





### 1.3 ABSORPTION AND BULK SPECIFIC GRAVITY

Based on test:       ASTM C-97-83  
"Standard Test Method for Absorption  
and Bulk Specific Gravity of Dimension Stone"

**No. of Specimens**

@Test:               3 (2 Consolidants, 1 Control)  
TOTAL:               9

**TIME REQUIRED**

Consolidation:       21 days  
Test:                   1 day  
TOTAL:                22 days

#### *Significance and Use*

These test methods are useful in indicating differences in absorption between the various dimension stones. These test methods also provide one element in comparing stones of the same type.

### ABSORPTION

#### *Test specimens*

Test specimens may be cubes, prisms, cylinders, or any regular form with least dimension not under 5 cm. (2 in.) and the greatest dimension not over 7.6 cm. (3 in.) but the ratio of the volume to surface area shall not be less than 8 mm. (0.3 in.) nor greater than 1.4 cm. (0.5 in.). All surfaces shall be reasonably smooth. At least three specimens shall be prepared for each sample.

#### *Procedure*

Determine the weights of the specimens to the nearest 0.02 g.

Immerse the specimens completely in filtered or distilled water at  $20 \pm 5^{\circ}\text{C}$  ( $68 \pm 9^{\circ}\text{F}$ ) for 48 hours. At the end of this period remove them from the water bath one at a time, surface dry with a damp cloth, and weigh to the nearest 0.02 g.

#### *Calculations and report*

Calculate the weight percentage absorption for each specimen as follows:



$$\text{Absorption, weight \%} = [(B - A) / A] \times 100$$

where:

A = weight of the dried specimen, and

B = weight of the specimen after immersion.

Report the average of all the specimens from each sample as the absorption of the sample. The report shall state the highest and lowest values and the average.

## **BULK SPECIFIC GRAVITY**

### *Samples and test specimens*

Samples may be the same as those used for water absorption, or other samples may be selected. At least three test specimens for each sample shall be tested, and they shall conform to the same requirements in size, shape and preparation as stated in the previous test procedure.

### *Procedure*

When both absorption and bulk specific gravity are to be determined on the same specimens, weigh the saturated specimens suspended in filtered or distilled water at  $20 \pm 5^\circ\text{C}$  ( $68 \pm 9^\circ\text{F}$ ) immediately after the absorption tests are completed. Determine the suspended weights to the nearest 0.02 g. A satisfactory means of weighing specimens in water is to use a basket for suspending the specimens in a glass jar of water supported above a balance pan. Determine the weight of the basket when suspended in water to the same depth as when weighing the specimens. Subtract the weight of the basket to the nearest 0.02 g. from the combined weight of the specimen and basket. Carefully remove air bubbles clinging to the basket or specimen before recording the weight.

When the bulk specific gravity is measured on specimens other than those used for absorption, immerse the specimens in water for at least 1 hour or until air bubbles do not form on the specimens. Surface dry the specimens, weigh to the nearest 0.02 g., and return to water bath. Determine the weight in water before the specimens have stood in water for more than 5 minutes.

### *Calculation and report*

Calculate the bulk specific gravity as follows:

$$\text{Bulk specific gravity} = A / (B - C)$$

where:

A = weight of the dried specimen,

B = weight of the soaked and surface-dried specimen in air, and

C = weight of the specimen soaked in water.



Calculate the results to three decimal points and round off to two. Report the average, maximum and minimum values.

*Precision and bias*

Individual variations in a natural product may result in deviation from accepted values. A precision section will be added when sufficient data are available to indicate repeatability and reproducibility.



## 1.4 WATER VAPOR TRANSMISSION

**Based on Test:**      ASTM E96-80  
"Standard Test Method for Water Vapor  
Transmission of Materials"

**No. of Specimens**  
**@test:**                4  
**TOTAL:**                12

**TIME REQUIRED**  
**Consolidation:**      21 days  
**Test:**                    36 days  
**TOTAL:**                57 days

### *Significance and Use*

The purpose of this test is to obtain by means of a simple apparatus, reliable values of water vapor transfer through permeable and semi-permeable materials, expressed in suitable units. These values are for use in design, manufacture and marketing. A permeance value obtained under one set of conditions may not indicate the value under a different set of conditions. Therefore, the test conditions should be selected that most closely approach the conditions of use.

### *Terminology*

water vapor permeability - the time rate of water vapor transmission through unit area of flat material of unit thickness induced by unit vapor pressure difference between two specific surfaces, under specified temperature and humidity conditions.

water vapor transmission rate - the steady water vapor flow in unit time through unit area of a body, normal to specific parallel surfaces, under specific conditions of temperature and humidity of each surface.

### *Apparatus*

Test dish - test dish shall be of any noncorroding material, impermeable to water or water vapor. It may be of any shape. Light weight is desirable. The mouth of the dish shall be as large as practical. The desiccant or water area shall not be less than the mouth area. An external flange or ledge around the mouth, to which the





## 1.4 WATER VAPOR TRANSMISSION

**Based on Test:**       ASTM E96-80  
                              "Standard Test Method for Water Vapor  
                              Transmission of Materials"

**No. of Specimens**  
**@test:**               4  
**TOTAL:**             12

**TIME REQUIRED**  
**Consolidation:**   21 days  
**Test:**               36 days  
**TOTAL:**            57 days

### *Significance and Use*

The purpose of this test is to obtain by means of a simple apparatus, reliable values of water vapor transfer through permeable and semi-permeable materials, expressed in suitable units. These values are for use in design, manufacture and marketing. A permeance value obtained under one set of conditions may not indicate the value under a different set of conditions. Therefore, the test conditions should be selected that most closely approach the conditions of use.

### *Terminology*

water vapor permeability - the time rate of water vapor transmission through unit area of flat material of unit thickness induced by unit vapor pressure difference between two specific surfaces, under specified temperature and humidity conditions.

water vapor transmission rate - the steady water vapor flow in unit time through unit area of a body, normal to specific parallel surfaces, under specific conditions of temperature and humidity of each surface.

### *Apparatus*

Test dish - test dish shall be of any noncorroding material, impermeable to water or water vapor. It may be of any shape. Light weight is desirable. The mouth of the dish shall be as large as practical. The desiccant or water area shall not be less than the mouth area. An external flange or ledge around the mouth, to which the



specimen may be attached, is useful when shrinking or warping occurs. When the specimen area is larger than the mouth area, this overlay upon the ledge is a source of error. This overlay material should be masked as described so that the mouth area defines the test area. If a rim is provided around the ledge, it shall not be more than 6 mm. (1/4 in.) higher than the specimen as attached.

Test chamber - the room or cabinet where the assembled test dishes are placed shall have a controlled temperature and relative humidity. The temperature chosen shall be between 21 and 32°C (70 and 90°F) and shall be maintained constant within 0.6°C (1°F). The relative humidity shall be maintained at  $50 \pm 2\%$  except where extremes of humidity are desired. Both temperature and relative humidity shall be measured frequently, or preferably recorded continuously. Air shall be continuously circulated throughout the chamber, with a velocity sufficient to maintain uniform conditions at all test locations.

Balance and weights - the balance shall be sensitive to a change smaller than 1% of the weight change during the period when a steady state is considered to exist. The weights used shall be accurate to 1% of the weight change during the steady state period. For this usage, the balance must have a sensitivity of 1% of 10% or 0.1g. and the weights must be accurate to 0.1 g.

### *Materials*

Water - For the water method, distilled water shall be used in the dish.

Sealant - The sealant used for attaching the specimen to the dish, in order to be suitable for this purpose, must be highly resistant to the passage of water vapor (and water). It must not lose weight to, or gain weight from, the atmosphere in an amount, over the required period of time that would affect the test result more than 2%. It must not affect the vapor pressure in a water-filled dish.

### *Test specimens*

The test specimens shall be representative of the material tested. When the product is designed for use in only one position, three specimens shall be tested by the same method with the vapor flow in the designated direction. The overall thickness of each specimen shall be measured at the center of each quadrant to the nearest 0.05 mm. (0.002 in.) and the results averaged.

### *Attachment of Specimen to Test Dish*

Attach the specimen to the dish by sealing (and clamping if desired) in such a manner that the dish mouth defines the area of specimen exposed to vapor pressure in the dish. If necessary, mask the specimen's top surface, exposed to conditioned air so that its exposure duplicates the mouth shape and size and is directly above it. A template is recommended for locating the mask. Thoroughly seal the edges of the specimen to prevent the passage of vapor into, or out of, or around the specimen edges or any portion thereof. The same assurance must apply to any part of the specimen faces outside the defined area.



### *Procedure for Water Method*

Fill the test dish with distilled water to a level  $19 \pm 6$  mm. ( $3/4 \pm 1/4$  in.) from the specimen. The air space thus allowed has a vapor space resistance, but is necessary in order to reduce the risk of water touching the specimen when the dish is handled. Such contact invalidates a test on some materials such as paper, wood or other hygroscopic materials. The water depth shall not be less than 3 mm. ( $1/8$  in.) to ensure coverage of the dish bottom throughout the test.

Attach the specimen to the dish. Some specimens are likely to warp and break the seal during the test. The risk can be reduced by preconditioning the specimen, and by clamping it to the dish ledge (if one is provided).

Weigh the dish assembly and place it in the controlled chamber on a true horizontal surface. If a test specimen cannot tolerate condensation on the surface, the dish assembly shall not be exposed to a temperature that differs more than  $2.8^{\circ}\text{C}$  ( $5^{\circ}\text{F}$ ) from the control atmosphere to minimize the risk of condensation on the specimen.

### *Analysis of Results, Calculations*

The results of the rate of water vapor transmission may be determined either graphically or numerically.

Graphic analysis - Plot the weight against elapsed time, and inscribe a curve which tends to become straight. When a straight line adequately fits the plot of at least six properly spaced units, with due allowance for scale sensitivity, a nominally steady state exists, and the slope of the straight line is the rate of water vapor transmission.

Numerical analysis - A mathematical least square regression analysis of the weight as a function of time will give the rate of water vapor transmission. An uncertainty, or standard deviation rate, can also be calculated to define the confidence band. For very low permeability materials, this method can be used to determine the results after 30 to 60 days when using an analytical balance, with a sensitivity of  $\pm 1$  mg., even if the weight change does not meet the sensitivity requirement. Specimens analyzed in this manner must be clearly identified in this report.

Calculate the water vapor transmission, WVT, as follows:

$$\text{WVT} = G/tA = (G/t)/A$$

where:

In metric units:

G = weight change (from the straight line), g.,

t = time during which G occurred, h,

G/t = slope of the straight line, g/ (h  $\times$  m<sup>2</sup>),

A = test area (cup mouth area), m<sup>2</sup>, and

WVT = rate of water vapor transmission, g/(h  $\times$  ft<sup>2</sup>).



### 1.5 DEPTH OF PENETRATION

**Based on Test** "A New Method for Determining the Depth of Penetration of Consolidants Using Iodine Vapor"

**No. of Specimens**

**@ test:** 3 (2 Consolidants)

**TOTAL:** 6

**TIME REQUIRED**

**Consolidation:** 21 days

**Test:** 1 day

**TOTAL:** 22 days

Based on Test "A New Method for Determining the Depth of Penetration of Consolidants into Stone Using Iodine Vapor"(Getty Conservation Institute).

#### *Significance and Use*

This test measures the depth of penetration of consolidants in light colored stones (i.e. light sandstones, limestone, tuff, etc.), useful in indicating differences in depth of penetration of consolidants in stones. This test was developed by Rakesh Kumar and William S. Ginnel at the Getty Conservation Institute.

#### *Specimens*

Test specimens may be cubes, prisms, cylinders or any regular form with least dimensions not under 5 cm. (2 in.). All the surfaces must be reasonably smooth. At least three specimens shall be prepared for each sample.

#### *Procedure*

The test must be carried out as follows:

1. Treat the stone specimens. Allow sufficient time for cure.
2. Expose the treated stone or its vertical section to iodine vapor in a closed glass chamber for about 10-15 minutes ( if the concentration of the consolidant is below 1-2% the test may require more time for exposure ).
3. Measure the area of distance of the colored (yellow or light brown) area.





When the stones are exposed to the iodine vapor in the closed chamber, the iodine is physically absorbed on the surface of the consolidant and produces a yellow or light brown color. Since the iodine vapor is not physically absorbed and does not react with the stone, only the areas consolidated with the organic compound will turn dark yellow or light brown leaving the unconsolidated areas the same color as the unconsolidated stone.



## 1.6 ACCELERATED WEATHERING TEST

**Based on Test:** ASTM G-53-88 "Standard Practice for Operating Light-and Water-Exposure Apparatus for Exposure of Non-metallic Materials"

**No. of Specimens**

**@ test:** 2 (2 Consolidants, 1 Control)

**TOTAL:** 6

**TIME REQUIRED**

**Consolidation:** 21 days

**Test:** 14 days

**TOTAL:** 35 days

### *Significance and Use*

To simulate the damaging effects of sunlight on a material, it is necessary to simulate the UV lengths of sunlight. The best method to simulate the effects of sunlight is to reproduce the shortest of the UV wave lengths, or the UV-B. To simulate the effects of outdoor wetness, it is necessary to produce hot condensation. The QUV weatherometer has the capability of reproducing the effects of sunlight and outdoor wetness attacks by exposing samples to UV-B light and hot condensation cycles. It is impossible to estimate how many cycles of exposure in the weatherometer equals a month of exposure to outdoor weather conditions, and the sensitivity of materials to UV-radiation. In general, however, the exposure of samples to UV-light and condensation cycles for 14 days will simulate the effects of exposure to sunlight and outdoor wetness over extended period of time, and provide a reasonable estimate of the resistance of the tested materials to sunlight and outdoor wetness.

### *Specimens*

The samples must be approximately 0.25 cm. thick and no less than (7.5 x 5)cm.

### *Procedure*

1. Place the specimens in the sample racks and insert the racks in the weatherometer.



2. Calibrate the UV exposure temperature to 65°C, and the condensation exposure to 40°C at four hour cycles (i.e., three cycles each per 24 hours).
3. Turn the weatherometer on and monitor for 14 days.
4. Remove the samples from the weatherometer and observe change in color and/or appearance by the standard practice for observing color differences of opaque materials (ASTM D1729-89), Record the color change by Munsell notations or the CIELAB system.



### 1.7 SODIUM SULPHATE CRYSTALLIZATION TEST

**Based on test:** BRE Sodium Sulphate Crystallization Test

**No. of Specimens**

**@ test:** 4 (2 Consolidants, 1 Control)

**TOTAL:** 12

**TIME REQUIRED**

**Consolidation:** 21 days

**Test:** 15 days

**TOTAL:** 36 days

Based on standard BRE "Sodium Sulfate Crystallization Test" (Building Research Establishment).

#### *Significance and Use*

The purpose of this test is to determine the resistance of stones to sodium sulfate crystallization. The test measures the weight change, and deterioration rate of stone samples exposed to repeated cycles of sodium sulfate crystallization.

#### *Procedure*

The test must be carried out as follows:

1. Make up a stock solution of sodium sulfate dissolving 1.4 kg. of sodium sulfate decahydrate in 8.6 liters of water, or by dissolving any hydrate of sodium sulfate in water until the specific gravity of the solution is 1.055 at 20°C. Approximately 2 liters will be needed to complete the test for each sample. The temperature of the solution should be maintained at  $20 \pm 0.5^\circ\text{C}$  throughout the test.
2. Using a suitable saw, cut a representative number of 4 cm. cubes of all the stone to be tested. No fewer than four cubes of each stone should be tested, but unless the stone is particularly variable a maximum of six should be difficult.
3. Remove any loose material by washing the water, and dry the samples at  $103 \pm 20^\circ\text{C}$  to constant weight (this can be achieved overnight in a ventilated oven).





4. Remove the samples from the oven. place them in a desiccator, and allow them to cool to  $20 \pm 2^{\circ}\text{C}$ . Weigh them to  $\pm 0.01$  g. ( $W_o$ ).
5. Place each sample in a 250 ml. container and cover with the fresh sodium sulfate solution to a depth of about 8 mm.. Leave for 2 hours during which time the temperature of the sample and solution should be kept at  $20 \pm 0.5^{\circ}\text{C}$ . When the samples have been soaking for 1.5 hours, place a shallow tray containing 300 ml. of water in the over (It was found empirically in the past that drying the samples in an oven which was initially humid improved the resolution of the test).
6. After a total of 2 hours of soaking, remove the samples from the solution and put them in the oven on wire racks. Dry the samples for 16 hours at  $103 \pm 2^{\circ}\text{C}$ .
7. Remove the samples from the oven and allow them to cool to  $20 \pm 2^{\circ}\text{C}$ . Steps 5-7 constitute one cycle of the test.
8. Repeat steps 5 to 7 until 15 cycles have been completed.
9. Weigh the samples ( $W_f$ ). Calculate the percentage increase in weight from the following equation:

$$\text{increase in weight (\%)} = 100 (W_f) / W_o$$

10. Calculate the mean percentage increase in weight for each set of samples.



## 1.8 SHEAR STRENGTH

**Based on Test:** ASTM D905-89  
"Standard Test Method for Strength Properties of  
Adhesive Bonds by Compression Loading"

**No. of Specimens**  
**@ test:** 4 (2 Consolidants, 1 Control)  
**TOTAL:** 12

**TIME REQUIRED**  
**Consolidation:** 21 days  
**Test:** 1 day  
**TOTAL:** 23 days

### *Significance and Use*

It cannot be assumed that this test method measures the true shear strength of the adhesive bond. Many factors interfere or bias the measurement including the strength of the material, the specimen, the shear tools themselves, and the rate of loading. The failure of the material is common in joints made with very strong adhesives. Although high material failure is normally desired, when it occurs, the measured strength is lower than the true adhesive bond strength.

The rate of loading affects the strength of an adhesive bond according to the adhesive's rheological properties. The more viscoelastic or plastic the adhesive, the greater the effect. The bond strengths can be measured over a range of loading rate from 0.015 to 0.5 in./min. with no apparent effect. Thermoplastic adhesives like polyvinyl acetate, hot melts, and elastomer-based adhesives exhibit a broad range of elastic, viscoelastic, and plastic behaviors. Their bond strength will be affected to varying degrees by changing the loading rate. Generally, increasing the rate, increases the measured strength.

This test method may be used for comparing and selecting adhesives, however, such comparisons must be made with caution since the measured strength of some adhesives may be different in different types of joints.

### *Apparatus*

The testing machine shall have a capacity of not less than 6810 kg. (15,000 lb) in comparison and shall be fitted with a shearing tool containing a self-aligning seat to ensure the uniform lateral distribution of the load. The machine



shall be capable of maintaining uniform rate of loading such as the load may be applied with a continuous motion of the movable head to a maximum load at a rate of 5 mm. (0.2 in.)/ min., with a permissible variation of  $\pm 25\%$ . The shearing machine shall be located in an atmosphere such that the moisture content of the specimens developed under the conditions prescribed is not noticeably altered during the test.

#### *Preparation of specimens*

Cut the specimens so that the bedding (or rift) is parallel to the direction of the loading during the test. The two blocks for each assembly shall be joined to allow a 0.5 cm. margin between the upper and lower face of each block. Take care in preparing the specimens to make the loaded surfaces smooth and parallel to each other and perpendicular to the height. Measure the width and length of the specimen at the glue line to the nearest 0.25 mm. (0.01 in.) to determine the shear area.

#### *Procedure*

Place the test specimen in the shearing tool so that the load may be applied with a continuous motion of the movable head at a rate of 5 mm. (0.2 in.)/ min. to failure as described above.

#### *Calculation and report*

Calculate the shear stress at failure in kilopascals (or pounds-force per square inch) based on the glue line area between the two lamination measured to the nearest  $0.06 \text{ cm}^2$  ( $0.01 \text{ in.}^2$ ), and report for each specimen together with the estimated percentage of material failure.

#### *Precision and bias*

**Precision** - Precision has two components : repeatability at a given site and reproducibility between test sites. The precision of this test method is affected by many factors including, but not limited to: 1) the material type, 2) the grain direction or bedding planes, 3) the condition of the shear tool, 4) the precision of the testing machine, and 8) the operator. When the specimen fails primarily in the material tested the normal variability of the material affects precision.

**Bias** - The difference between the true shear strength of the adhesive bond and the strength measured by a method that is repeatable. Bias arises from the design, method, rate of loading the specimen, and from the strength of the material.



## 1.9 QUANTITATIVE ANALYSIS OF SOLUBLE SALTS

### *Significance and Use*

The qualitative and quantitative analysis of soluble salts, performed at a professional chemical laboratory, can determine the quantity of soluble ions present in the material with a reasonable degree of accuracy. To obtain the most accurate results possible, the specimen examined must be a representative sample of material from the site which has undergone deterioration. The test determines the content of soluble ions ( $\text{Cl}^-$ ,  $\text{NiO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) most commonly found in deteriorated stones. The analytical methods for determining the presence of soluble ions include atomic absorption for calcium and nitrates, gravimetric analysis for sulfates, the brucine method for nitrates, and titration with silver nitrate for chlorides.





## APPENDIX C

### EXPERIMENTAL PROGRAM DATA

The results of the experimental program for the evaluation of the consolidation and adhesive repair of samples of volcanic tuff from the Old Stone Church at Mission San Juan Capistrano are recorded below on standardized test sheets. The specimens were consolidated with an aliphatic epoxy resin solution composed of a mixture of Eponex 1510 (Shell), Jeffamine D-230 (Texaco) in a 10% solution of toluene and isopropanol, and an ethyl silicate, Stone Strengtheners OH (ProSoCo). An epoxy adhesive, a mixture of Epon 828 and Jeffamine D-230, was injected into assemblies of volcanic tuff consolidated with the epoxy resin solution and ethyl silicate. All tests were performed with two sets of consolidated specimens, and one set of unconsolidated or control specimens, and the results subjected to statistical analysis.



**Table 1.1** Modulus of Rupture of Specimens Treated with Epoxy Resin and Ethyl Silicate and Unconsolidated Specimens, based on ASTM C99-87, "Standard Test for Modulus of Rupture of Dimension Stone."

MODULUS OF RUPTURE			
SPECIMEN TYPE		R (psi)	R (kPa)
E P O X Y	1.01	475	3278
	1.02	337	2325
	1.03	413	2850
S I L I C.	2.01	447	3084
	2.02	271	1870
	2.03	504	3478
U N C O N.	3.01	375	2588
	3.02	416	2870
	3.03	337	2325

**Sample size** = (3.9 x 1.9 x 7.9) in., (10 x 5 x 20) cm.

**Sample area** = 7.68 in.<sup>2</sup>, 19.5 cm.<sup>2</sup>.



**Table 1.2.** Statistical Analysis of Results of Modulus of Rupture Test.

SPECIMEN TYPE	x	s	t
EPOXY	408	69.04	0.32
SILIC.	407	121.45	0.16
UNCONSOL.	376	39.5	0.36

$$F_{1,2} = 3.06$$

$$F_{2,3} = 9.38$$

$$F_{1,3} = 3.06$$

critical value for t-test = 4.30

critical value for F-test = 39.0



**Table 2.1.** Compressive Strength of Specimens Treated with Epoxy Resin and Ethyl Silicate and Unconsolidated Specimens, based on ASTM C170-97, "Standard Test Method for Compressive Strength of Dimension Stone."

COMPRESSIVE STRENGTH - RESULTS			
SPECIMEN TYPE		C (psi)	C (kPa)
E P O X Y	A1.01	343	2366
	A1.03	476	3284
	C1.01	437	3015
	C1.02	262	1808
S I L I C.	A2.01	458	3160
	A2.02	366	2525
	C2.01	455	3140
	C2.02	488	3367
U N C O N.	A3.01	438	3022
	A3.02	493	3402
	C3.01	395	3726
	C3.02	488	3367





### Dimensions of samples for compressive strength test

**Sample size** = (1.5 x 1.5 x 1.4) in., (3.8 x 3.8 x 3.6) cm.

**Surface area** = 2.25 in.<sup>2</sup>, 12.9 cm.<sup>2</sup>

**Table 2.2.** Statistical Analysis of Results of Compressive Strength Test.

SPECIMEN TYPE	x	s	t
EPOXY	379	96.19	0.44
SILIC.	441	52.66	0.01
UNCONS.	453	47.04	0.36

$$F_{1,2} = 3.33$$

$$F_{2,3} = 0.0004$$

$$F_{1,3} = 4.18$$

critical value for t-test = 3.18

critical value for F-test = 15.44



**Table 3.1.** Absorption and Bulk Specific Gravity of Specimens Consolidated with Epoxy Resin and Ethyl Silicate and Unconsolidated Specimens, based on ASTM C97-83, "Standard Test Method for Absorption and Bulk Specific Gravity of Dimension Stone."

ABSORPTION AND BULK SPECIFIC GRAVITY - RESULTS			
SPECIMEN TYPE		ABSORPTION (Wt %)	BULK SPECIFIC GRAVITY (g.)
E P O X Y	A1.01	17.39	1.84
	A1.02	18.14	1.88
	A1.03	19.01	1.88
S I L I C.	A2.01	15.73	1.89
	A2.02	15.59	1.92
	A2.03	15.01	1.91
U N C O N.	A3.01	19.52	1.89
	A3.02	20.2	1.85
	A3.03	28.39	1.85



**Table 3.2 Statistical Analysis of Results of Absorption Test**

SPECIMEN TYPE	x	s	t
EPOXY RESIN	18.2	0.81	0.72
ETHYL SILICATE	15.4	0.34	0.75
UNCONSOLIDATED	19.5	4.94	0.64

$$F_{1,2} = 4.48$$

$$F_{2,3} = 165.99$$

$$F_{1,3} = 37.08$$

**Table 3.3 Statistical Analysis of Results of Bulk Specific Gravity Test**

SPECIMEN TYPE	x	s	t
EPOXY RESIN	1.87	0.02	0.67
ETHYL SILICATE	1.91	0.02	0.50
UNCONSOLIDATED	1.86	0.03	0.50

$$F_{1,2} = 1.67$$

$$F_{2,3} = 2.00$$

$$F_{1,3} = 1.20$$

critical value for t-test = 4.30

critical value for F-test = 39.0



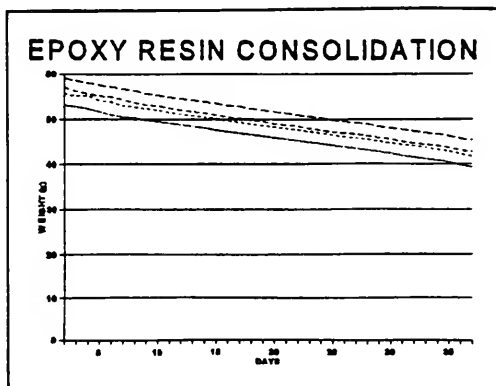
**Table 4.1** Water Vapor Transmission Results, Based on ASTM E96-80, "Standard Test for Water Vapor Transmission of Materials."

WATER VAPOR TRANSMISSION - RESULTS			
SPECIMEN TYPE		WEIGHT CHANGE (g/tm <sup>2</sup> )	WVT (g/t)
E P O X Y	1.1	0.36	0.007
	1.2	0.37	0.007
	1.3	0.37	0.007
	1.4	0.36	0.007
S I L I C.	2.1	0.39	0.008
	2.2	0.37	0.008
	2.3	0.38	0.008
	2.4	0.37	0.008
U N C O N S.	3.1	0.42	0.008
	3.2	0.42	0.008
	3.3	0.49	0.01
	3.4	0.48	0.01

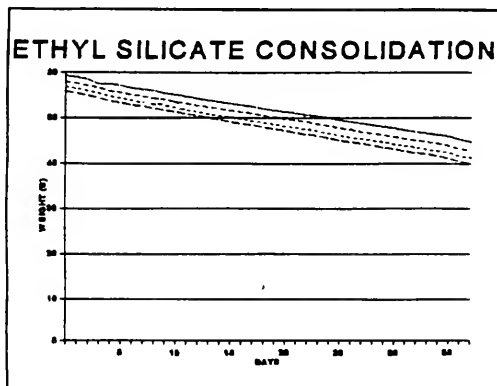




**Table 4.2** Water Vapor Transmission of Specimens Consolidated with Epoxy Resin based on ASTM E96-80, "Standard Test for Water Vapor Transmission of Materials."

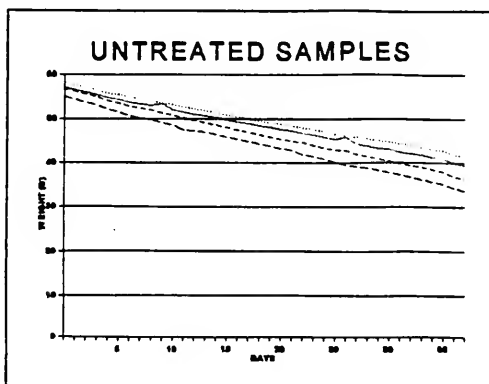


**Table 4.3** Water Vapor Transmission of Specimens Consolidated with Ethyl Silicate based on ASTM E96-80, "Standard Test for Water Vapor Transmission of Materials."





**Table 4.4** Water Vapor Transmission of Unconsolidated Specimens, based on ASTM E96-80, "Standard Test for Water Vapor Transmission of Materials."





**Table 5.1** Depth of Penetration of Treatments in Specimens Consolidated with Epoxy Resin and Ethyl Silicate, based on Iodine Vapor Test.

DEPTH OF PENETRATION - RESULTS		
SPECIMEN TYPE		DEPTH OF PENETRATION (cm.)
E P O X Y	1.01	0.50 > 1.0
	1.02	0.50 > 1.0
	1.03	0.50 > 1.0
S I L I C.	2.01	0.75 > 1.0
	2.02	0.75 > 1.0
	2.03	0.75 > 1.0

**Table 5.2** Statistical analysis of depth of penetration test

SPECIMEN TYPE	Mean value (x)	Standard deviation (s)
EPOXY RESIN	0.75	0
ETHYL SILICATE	0.88	0



**Table 6.1.** Sodium Sulphate Crystallization of Specimens Consolidated with Epoxy Resin and Ethyl Silicate and Unconsolidated Specimens, based on BRE "Sodium Sulphate Crystallization Test" (  $f$  = cycle;  $f_n = 100 \times W_t/W_o$  (% increase in weight))

SODIUM SULFATE CRYSTALLIZATION TEST - RESULTS						
SPECIMEN		$W_o$	$W_{f1}$	Wt %	$W_{f2}$	Wt %
E P O X Y	S1.01	85.3	86.5	+1.9	88.5	+3.7
	S1.02	88.1	90.3	+2.3	90.2	+4.1
	S1.03	85.7	87.5	+2.1	87.5	+3.7
	S1.04	84.8	86.6	+2.1	86.6	+3.7
S I L I C.	S2.01	96.3	96.2	+0.1	85.2	+3.7
	S2.02	85.1	85.2	+0.0	85.2	+0.8
	S2.03	86.0	86.1	+0.1	86.1	+0.9
	S2.04	84.4	84.5	+0.1	84.5	+0.9
U N C O N.	S3.01	93.8	94.5	+1.1	94.8	+2.6
	S3.02	101	101.8	+1.1	94.8	+2.6
	S3.03	90.0	91.4	+1.4	91.4	+3.1
	S3.04	96.3	97.4	+1.1	97.4	+2.6





**Table 7.1.** Shear Strength of Adhesive Bonds of Assemblies Injected with Epoxy Resin Adhesive, based on ASTM D905-89, "Standard Method for Strength Properties of Adhesive Bonds by Compressive Loading.

SHEAR STRENGTH - RESULTS					
SPECIMEN TYPE		C (psi)	C (kPa)	Width of Break (in.)	Width of Break (cm.)
E P O X Y	1.01	137	945	0 - 0.6	0 - 0.5
	1.02	133	918	0 - 0.4	0 - 1.0
	1.03	207	1428	0 - 0.1	0 - 0.3
	1.04	222	1532	0 - 0.4	0 - 1.0
S I L I C.	2.01	141	973	0 - 0.2	0 - 0.5
	2.02	222	1532	0 - 0.6	0 - 1.5
	2.03	178	1228	0 - 0.3	0 - 0.8
	2.04	188	1297	0 - 0.5	0 - 1.3
U N C O N.	3.01	176	1214	0 - 0.2	0 - 0.5
	3.02	156	1076	0 - 0.1	0 - 0.3
	3.03	144	994	0 - 0.3	0 - 0.8
	3.04	119	821	0 - 0.4	0 - 1.0



**assembly size** = 2 (1.4 x 2.8 x .6) in., 2 (3.6 x 7.1 x 1.5) cm.

**width of joint** = 0.02 in., 0.05 cm.

**area of adhesive** = (.98 x 1.38) in., (2.5 x 3.5) cm.

The assemblies consisted of two pieces of volcanic tuff, (3.6 x 7.1 x 1.5) cm. in size, joined by two sticks, 0.05 cm. thick. The joints were then sealed on three sides with paraffin wax. The joints were injected with epoxy adhesive with a 16 g 1/2 needle and syringe.

**Table 7.2.** Statistical Analysis of Results of Shear Strength Test.

SPECIMEN TYPE	x	s	t
EPOXY	174	46.3	1.22
SILIC.	176	34.1	0.04
UNCONS.	148	23.8	1.03

$$F_{1,2} = 1.84$$

$$F_{2,3} = 2.04$$

$$F_{1,3} = 3.76$$

critical value for t-test = 3.18

critical value for F-test = 15.44 ,



**Table 8.** Quantitative Analysis of Soluble Ions Present in Sample of Deteriorated Volcanic Tuff.

QUANTITATIVE ANALYSIS OF SOLUBLE IONS - RESULTS					
SOLUBLE ION	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>
PPM	50	131	750	202	300
WEIGHT %	0.005	0.013	0.075	0.02	0.03



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12. C. Selwitz, *Epoxy Resins in Stone Conservation* (Marina del Rey, Ca: Getty Conservation Institute, 1991), 5.
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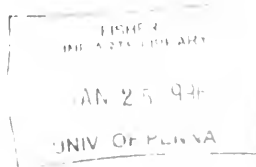


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